
Tutorial 13. CVD Synthesis of Carbon Nanotubes

Introduction

The purpose of this tutorial is to illustrate the use of the species transport model for simulating the chemical vapor deposition (CVD) synthesis of carbon nanotubes.

This tutorial demonstrates how to do the following:

- Define the material and set the mixture composition.
- Define volumetric reactions.
- Define surface reactions.
- Setup the solver and perform iterations.
- Check the convergence.
- Examine the results.
- Perform post-processing of surface reactions.

Prerequisites

This tutorial assumes that you have little experience with FLUENT but are familiar with the interface.

Problem Description

Chemical vapor deposition is one of the most efficient methods of synthesizing carbon nanotubes. This tutorial illustrates the application of CVD using a multi-step chemical reaction to predict the yield of carbon nanotubes. These multiwalled carbon nanotubes are produced from Xylene-based CVD reactors. In the present tutorial, two-step Xylene decomposition in the gas phase and catalytic decomposition of hydrocarbons are modeled, as reported by Kazunori [1].

A reactor for the production of nanotubes is shown in Figure 13.1.

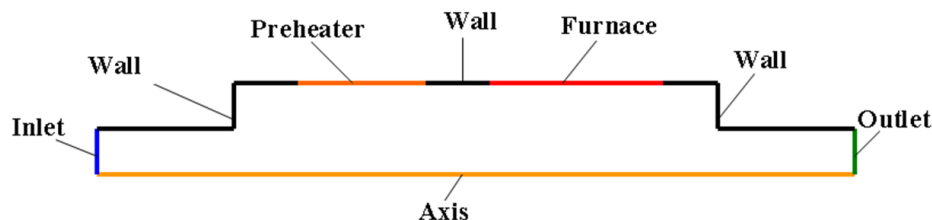
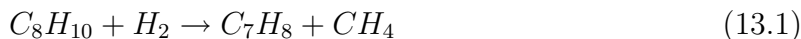


Figure 13.1: Problem Schematic

The process gases Xylene (C_8H_{10}), Hydrogen (H_2), and the carrier gas Argon (Ar) enter the reactor at 300 K through the Inlet. These gases flow over the hot preheater, which is maintained at 513 K. The preheater is used to avoid flow turbulence caused by buoyancy effects. Laminar flow conditions are necessary to synthesize CVD products of better quality. In practice, before nanotube synthesis, the Fe particles are produced on the furnace wall through the thermal decomposition of Ferrocene. This catalyst preparation step is not modeled here. The carrier gas scavenges oxygen and prevents the carbon from reacting to form carbon dioxide. The reactor is operated at 250 Pa overpressure to prevent oxygen influx.

The carbon solid ($C_{<s>}$) deposition rate on is governed by the following reactions:

Volumetric Reactions



Wall Surface Reactions



As mentioned previously, the inlet gas is a mixture of Xylene (C_8H_{10}), Hydrogen (H_2), and Argon (Ar). In this mixture, the mass fractions of Xylene and Hydrogen are 0.03359

and 0.1, respectively. The mixture velocity at the Inlet is 0.064517 m/s. The furnace wall is maintained at 973 K, and an adiabatic condition is used at the other walls.

In this tutorial, the surface deposition rate of $C_{<s>}$ along the furnace is simulated and examined. The purpose of this tutorial is to demonstrate the surface reaction capabilities of FLUENT .

Preparation

1. Copy the mesh file, CVD_synthesis.msh to your working folder.
2. Start the 2D double precision (2ddp) version of FLUENT .

Setup and Solution

Step 1: Grid

1. Read the mesh file, CVD_synthesis.msh.

File → **Read** → Case...

FLUENT will read the mesh file and report the progress in the console window. The console window will display the warning "The use of axis boundary conditions is not appropriate for a 2D/3D flow problem. Please consider changing the zone type to symmetry or wall, or the problem to axisymmetric". In step 2.1, we will choose the axisymmetric solver.

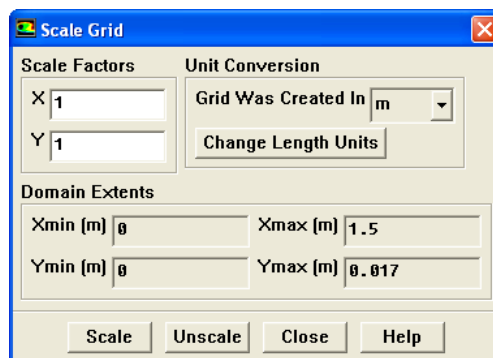
2. Check the grid.

Grid → Check...

This procedure checks the integrity of the mesh. Make sure that the reported minimum volume is a positive number.

3. Check the scale of the grid.

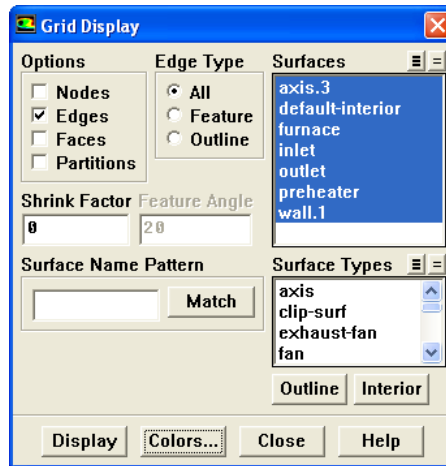
Grid → Scale...



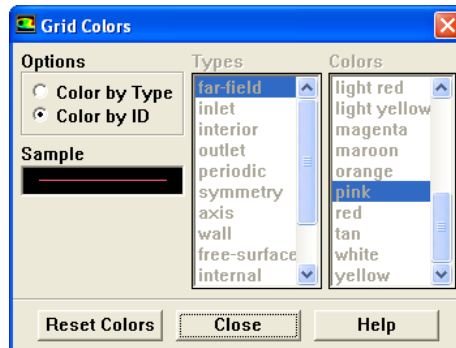
Check the domain extents to see if they correspond to the actual physical dimensions. Else the grid needs to be scaled with proper units.

4. Display the grid.

Display → Grid



- (a) Click Colors...



- i. Enable Color by ID in the Options list.
- ii. Close the Grid Colors panel.

- (b) Click Display and close the Grid Display panel.

We can use the right mouse button to check which zone number corresponds to each boundary. If you click the right mouse button on one of the boundaries in the graphics window, its zone number, name, and type will be printed in the FLUENT console window. This feature is especially useful when you have several zones of the same type and you want to distinguish between them quickly.



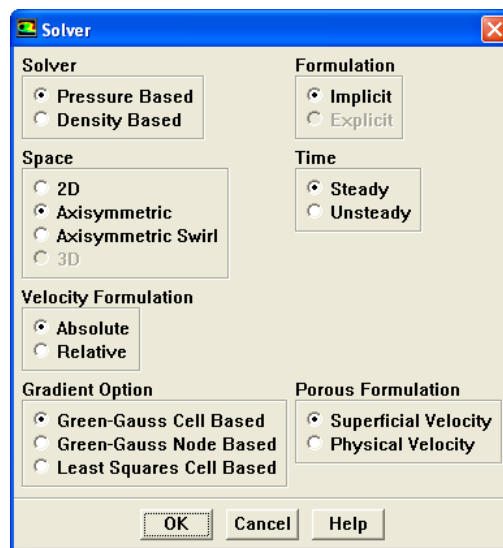
Figure 13.2: Grid Display

Step 2: Models

The problem is to be solved in the steady state with axisymmetric conditions.

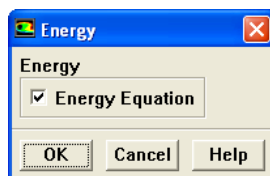
1. Enable the axisymmetric solver settings.

Define → Models → Solver...



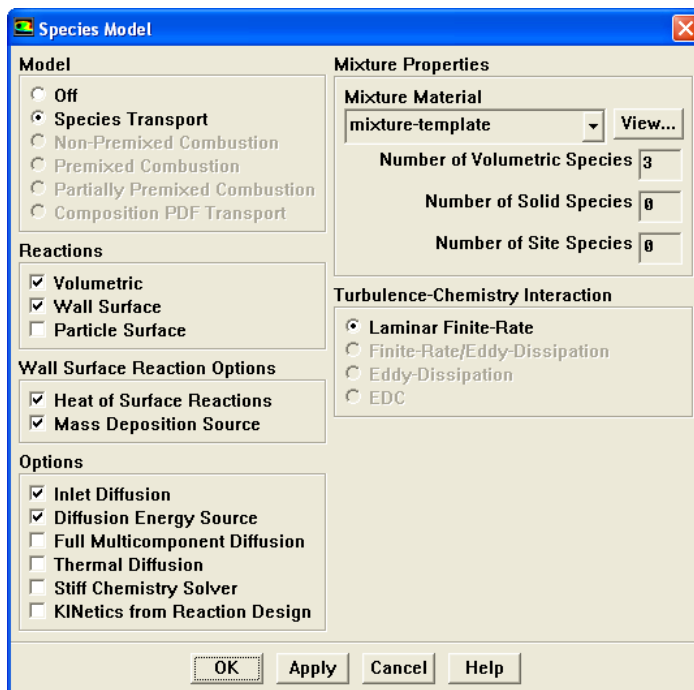
- (a) Enable Axisymmetric in the Space list.
 - (b) Click OK to close the Solver panel.
2. Enable heat transfer by activating the energy equation.

Define → Models → Energy...



- (a) Enable Energy Equation in the Energy group box.
 - (b) Click OK to close the Energy panel.
3. Enable Species transport and reactions.

Define → Models → Species → Transport & Reaction...



- (a) Enable Species Transport in the Model list.
- (b) Select Volumetric and Wall Surface in the Reactions group box.
- (c) Select Heat of Surface Reactions in the Wall Surface Reaction Options group box.

The heat release due to a wall surface reaction is, by default, ignored by FLUENT. You can, however, choose to include the heat release of a surface reaction by activating the Heat of Surface Reactions option in the Species Model panel and setting appropriate formation enthalpies in the Materials panel.

- (d) Select Mass Deposition Source in the Wall Surface Reaction Options group box.

Mass Deposition Source is selected because there is a certain loss of mass due to the surface deposition reaction, i.e., $C_{<s>}$ is being deposited out. If you were to do an overall mass balance without taking this fact into account, you would end up with a slight imbalance.

- (e) Retain the selection of Inlet Diffusion and Diffusion Energy Source in the Options list.

This includes the effect of enthalpy transport due to species diffusion in the energy equation, which contributes to the energy balance, especially for the case of Lewis numbers far from unity.

- (f) Click OK to close the Species Model.

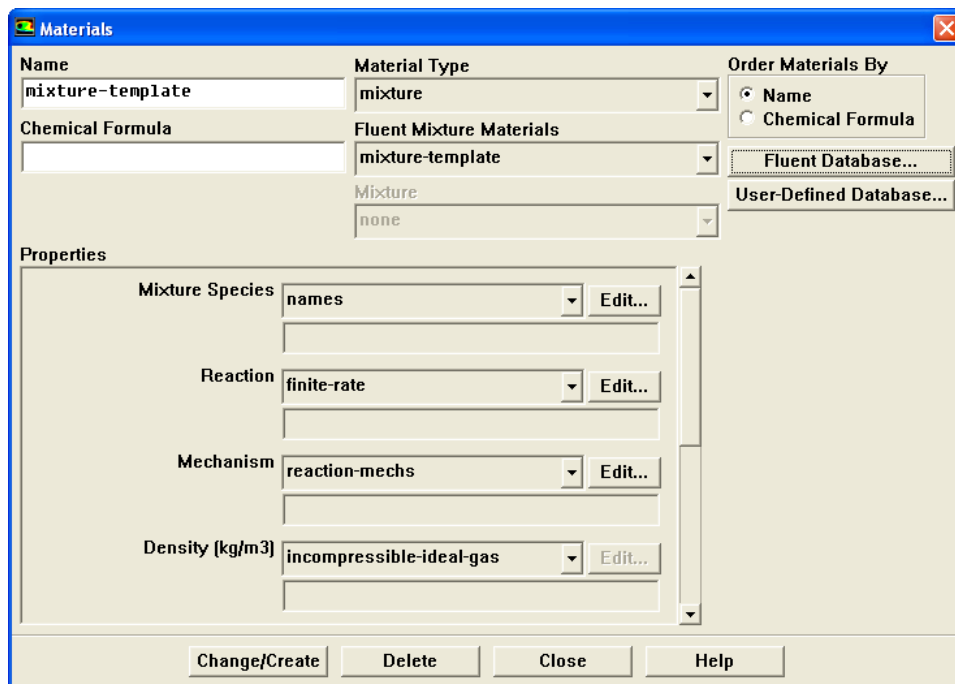
The console will list the properties that are required for the models that you have enabled. You will see an Information dialog box, reminding you to confirm the property values that have been extracted from the database.

- (g) Click OK in the information dialog box.

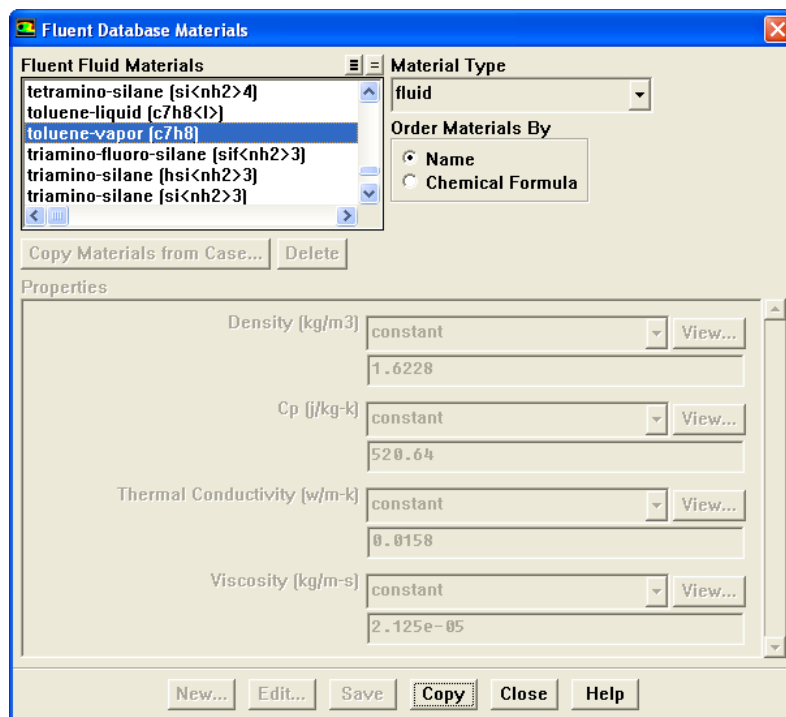
Step 3: Materials

1. Change the material properties.

→ Materials...

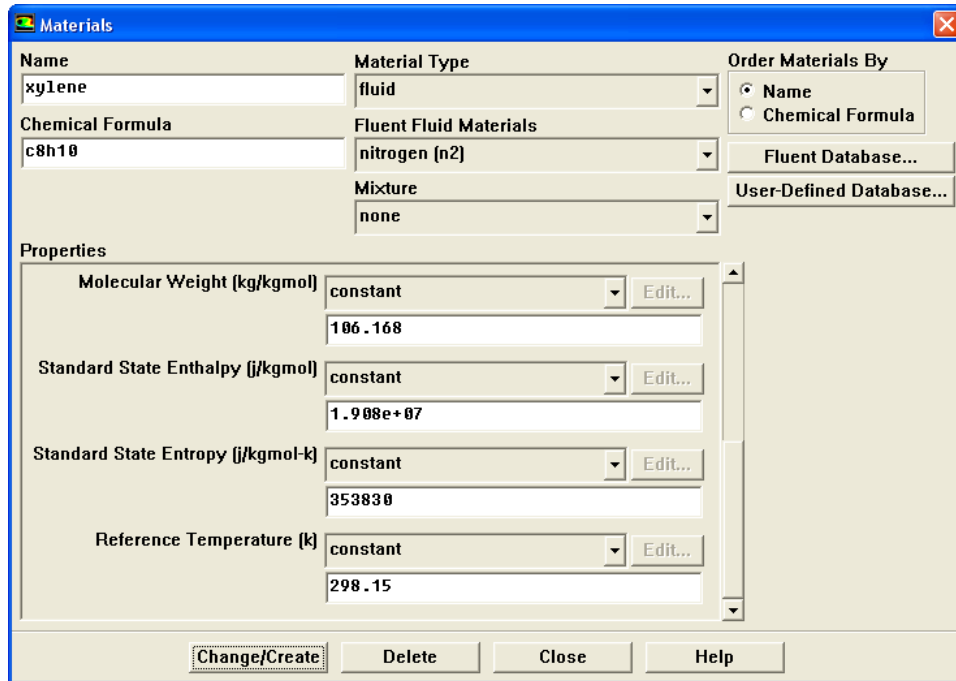


(a) Click Fluent Database... in the Materials panel.



- i. Select fluid in the Material Type drop-down list.
- ii. Select argon (ar), benzene-vapor (c6h6), carbon-solid ($c < s >$), hydrogen (h2), methane (ch4), and toluene-vapor (c7h8) in the Fluent Fluid Materials list.

- iii. Click Copy and close the Fluent Database Materials panel.
- (b) Define new material, xylene (c8h10).



- i. Select fluid from the Material Type drop-down list in the Materials panel.
- ii. Select nitrogen[n2] from the Fluent Fluid Materials drop-down list.
- iii. Select none from the Mixture drop-down list.
- iv. Enter xylene in the Name list.
- v. Enter c8h10 for Chemical Formula.
- vi. Specify the following for each of the properties:

Parameter	Value
Density	1.138
Cp	1282.901
Thermal Conductivity	0.0242
Viscosity	1.7894e-05
Molecular Weight	106.168
Standard State Enthalpy	1.908e+07
Standard State Entropy	353830
Reference Temperature	298.15

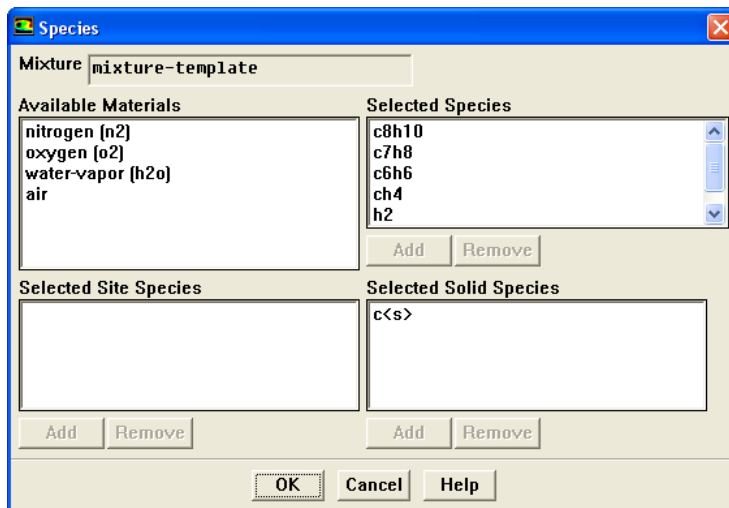
Ignore the Density parameter as the density will be set to incompressible-ideal-gas-law for mixture.

- (c) Click Change/Create to create the new material.
- (d) Click No in the Question panel when asked to overwrite.

(e) Set the mixture Composition.

- i. Select mixture in the Material Type drop-down list.
- ii. Click Edit... next to the Mixture Species in the Properties group box.

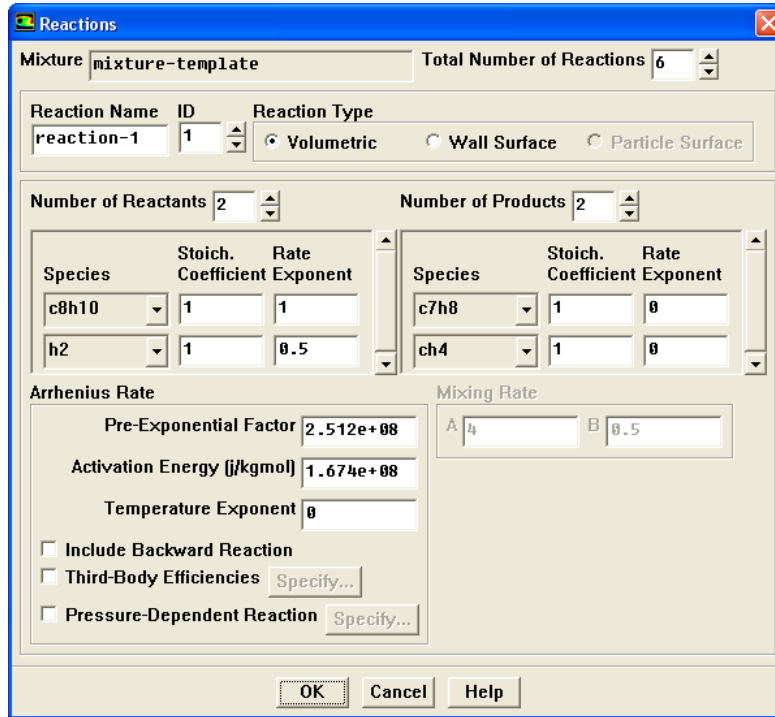
Here Selected Species, Selected Solid Species, and Selected Site Species represent the gas phase species, the bulk (or solid) species, and the surface-adsorbed (or site) species, respectively.



- iii. Select xylene[c8h10] in the Available Materials list and click Add in the Selected Species group box.
- iv. Select all the remaining species one by one and click Remove in the Selected Species group box.
- v. Select c7h8 in the Available Materials list and click Add in the Selected Species group box.
- vi. Similarly add c6h6, ch4, h2 and ar to the Selected Species list.
- vii. Select $c < s >$ in the Available Materials list and click Add in the Selected Solid Species group box.
- viii. Click OK to save the material composition.

Note: *The species should appear in the same order as shown in the above panel.*

(f) Set the mixture reactions.

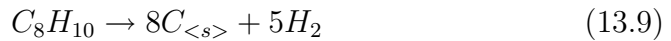


- i. Click Edit... next to the Reaction in the Properties group box.
- ii. Enter 6 for the Total Number of Reactions, and define the following reactions:

Volumetric Reactions



Wall Surface Reactions



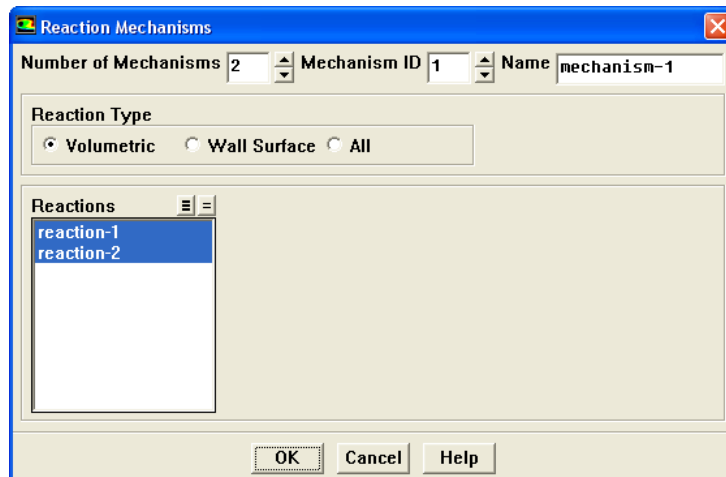
The parameters for the equations are as follows:

Parameter	Equation 13.1	Equation 13.2	Equation 13.3	Equation 13.4	Equation 13.5	Equation 13.6
Reaction Name	reaction-1	reaction-2	reaction-3	reaction-4	reaction-5	reaction-6
Reaction ID	1	2	3	4	5	6
Reaction Type	Volumetric	Volumetric	Wall Surface	Wall Surface	Wall Surface	Wall Surface
Number of Reactants	2	2	1	1	1	1
Species	c8h10, h2	c7h8, h2	c8h10	c7h8	c6h6	ch4
Stoich. Coefficient	c8h10 = 1 h2 = 1	c7h8 = 1 h2 = 1	c8h10 = 1	c7h8 = 1	c6h6 = 1	ch4 = 1
Rate Exponent	c8h10 = 1 h2 = 0.5	c7h8 = 1 h2 = 0.5	c8h10 = 1	c7h8 = 1	c6h6 = 1	ch4 = 1
Arrhenius Rate	PEF=2.512e+08 AE=1.674e+08 TE=0	PEF=1.259e+11 AE=2.2243e+08 TE=0	PEF=0.00034 AE=0 TE=0	PEF=0.00034 AE=0 TE=0	PEF=0.00034 AE=0 TE=0	PEF=0.008 AE=0 TE=0
Number of Products	2	2	2	2	2	2
Species	c7h8, ch4	c6h6, ch4	c<s>, h2	c<s>, h2	c<s>, h2	c<s>, h2
Stoich. Coefficient	c7h8 = 1 ch4 = 1	c6h6 = 1 ch4 = 1	c<s> = 8 h2 = 5	c<s> = 7 h2 = 4	c<s> = 6 h2 = 3	c<s> = 1 h2 = 2
Rate Exponent	c7h8 = 0 ch4 = 0	c6h6 = 0 ch4 = 0	c<s> = 0 h2 = 0	c<s> = 0 h2 = 0	c<s> = 0 h2 = 0	c<s> = 0 h2 = 0

Here, PEF = Pre-Exponential Factor, AE = Activation Energy, and TE = Temperature Exponent.

(g) Set the reaction mechanisms for the mixture.

i. Click Edit... next to the Mechanism in the Properties list.



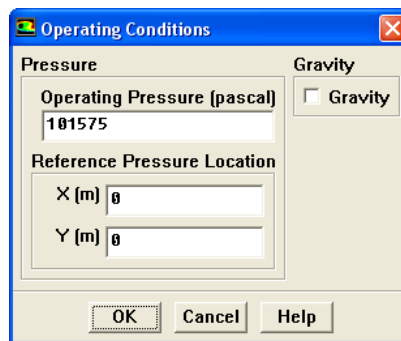
ii. Enter 2 for the Number of Mechanisms.

iii. Retain mechanism-1 for Name.

- iv. Enable Volumetric in the Reaction Type group box.
 - v. Select reaction-1 and reaction-2 in the Reactions list.
 - vi. Set the Mechanism ID to 2.
 - vii. Enable Wall Surface in the Reaction Type group box.
 - viii. Select reaction-3, reaction-4, reaction-5, and reaction-6 in the Reactions list.
 - ix. Click OK to save the mechanism definitions.
- (h) Retain the default settings for Density, Cp, Thermal Conductivity, Viscosity and Mass Diffusivity in the Materials panel.
- (i) Click Change/Create and close the Materials panel.

Step 4: Operating Conditions

Define → Operating Conditions...



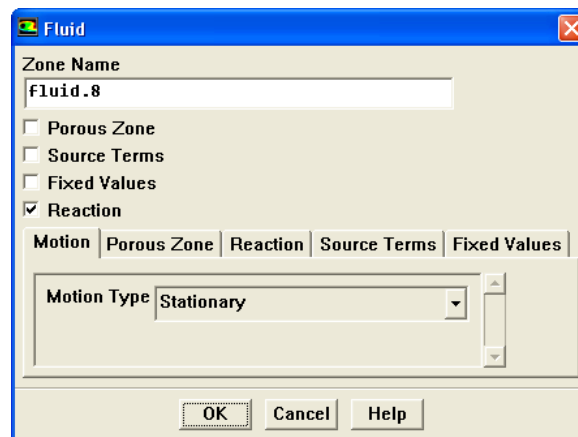
1. Enter 101575 pascal for Operating pressure.
2. Click OK to close the Operating Conditions panel.

Step 5: Boundary Conditions

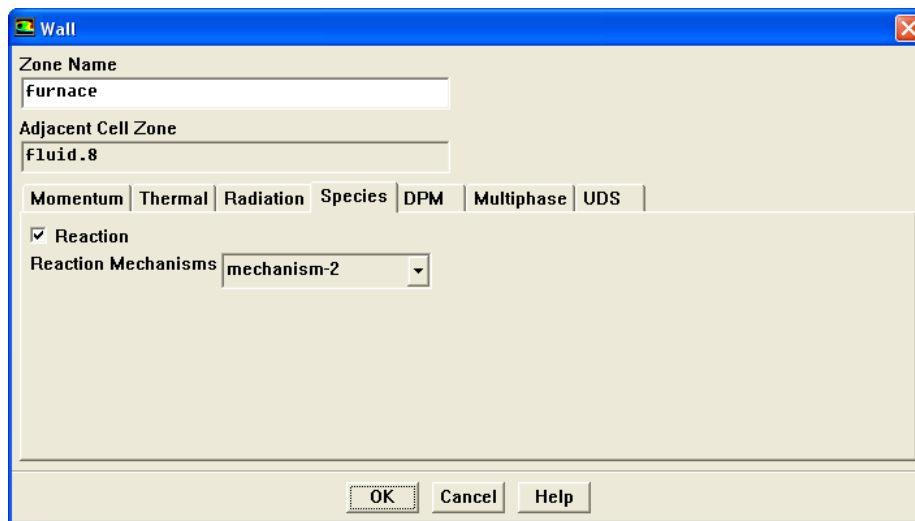
1. Set the boundary conditions.

Define → Boundary Conditions...

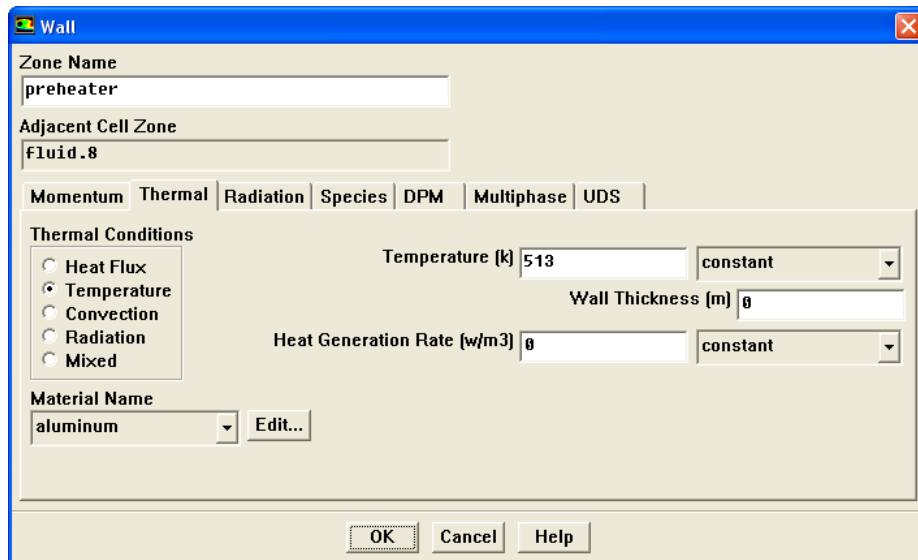
- (a) Select fluid.8 in the Zone list and click Set....



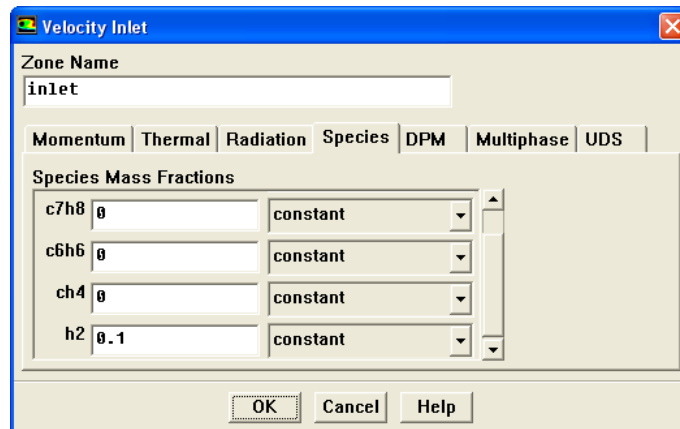
- i. Retain the default boundary conditions for fluid.8.
 - ii. Click OK to close the Fluid panel.
- (b) Select furnace in the Zone list and click Set....



- i. Retain the default conditions under Momentum tab.
 - ii. Click the Thermal tab.
 - iii. Select Temperature in the Thermal Conditions list and enter 973 K for the Temperature.
 - iv. Click the Species tab.
 - v. Enable the Reaction toggle button.
 - vi. Select the mechanism-2 from the Reaction Mechanisms drop-down list.
 - vii. Click OK to close the Wall panel.
- (c) Select preheater in the Zone list and click Set....

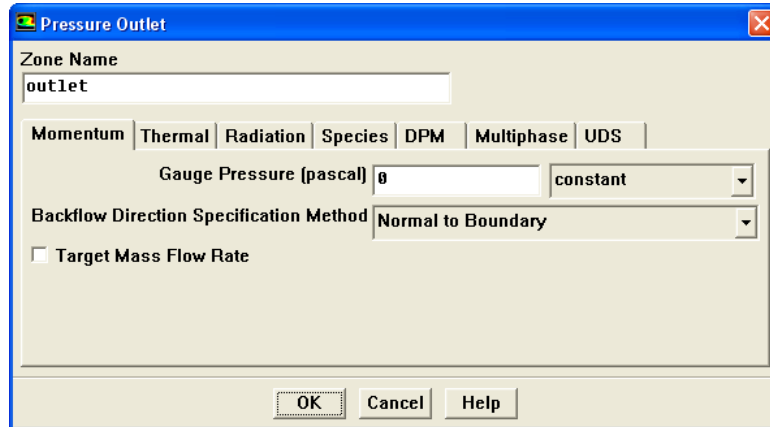


- i. Retain the default conditions under Momentum tab.
 - ii. Click the Thermal tab.
 - iii. Select Temperature in the Thermal Conditions list and enter 513 K for the Temperature.
 - iv. Click OK to close the Wall panel.
- (d) Select inlet in the Zone list and click Set....



- i. Click the Momentum tab.
- ii. Enter 0.064517 m/s for Velocity Magnitude.
- iii. Click the Thermal tab and enter 300 K for the Temperature.
- iv. Click the Species tab.
- v. Enter 0.03359 for c8h10 and 0.1 for h2.
- vi. Click OK to close the Velocity Inlet panel.

(e) Select outlet in the Zone list and click Set....



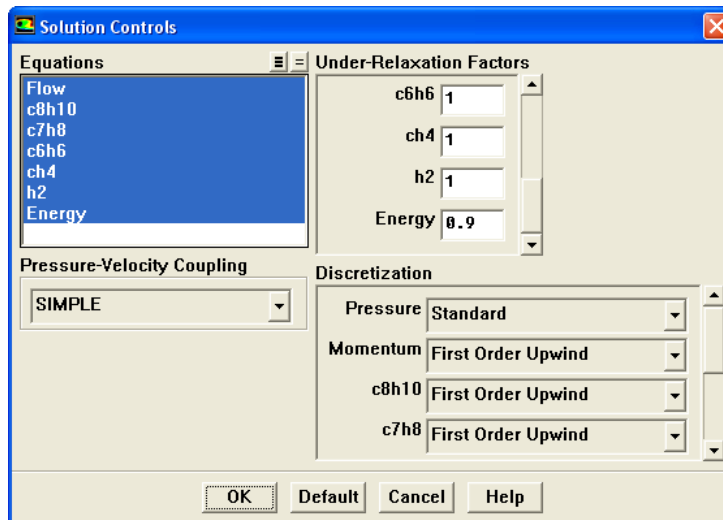
- i. Retain the default boundary conditions.
- ii. Click OK to close the Pressure Outlet panel.

(f) Close the Boundary Conditions panel.

Step 6: Solution

1. Set the solution parameters.

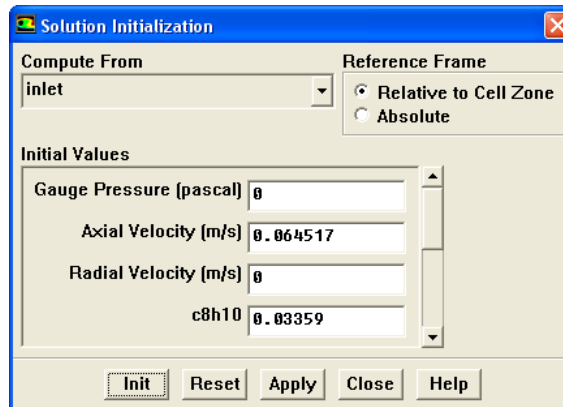
Solve → Controls → Solution...



- (a) Enter 0.5 and 0.9 for Momentum and Energy in the Under-Relaxation Factors group box.
- (b) Retain the default values for other parameters.
- (c) Click OK to close the Solution Controls panel.

2. Initialize the flow field.

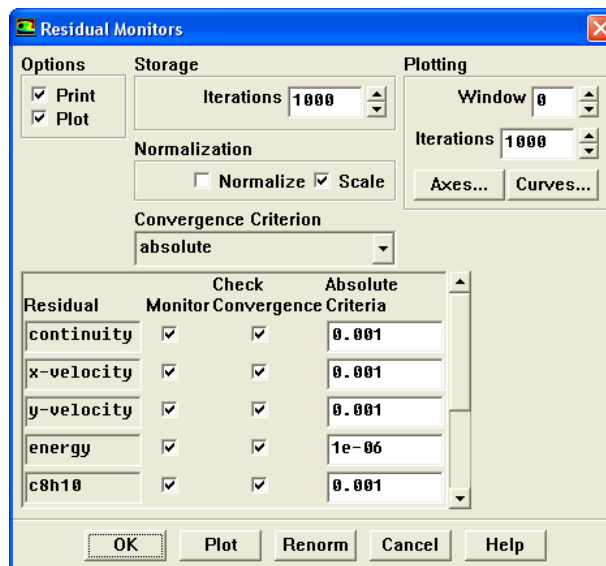
Solve → Initialize → Initialize...



- (a) Select inlet from the Compute From drop-down list.
- (b) Click Init and close the Solution Initialization panel.

3. Enable the plotting of residuals.

Solve → Monitors → Residual...



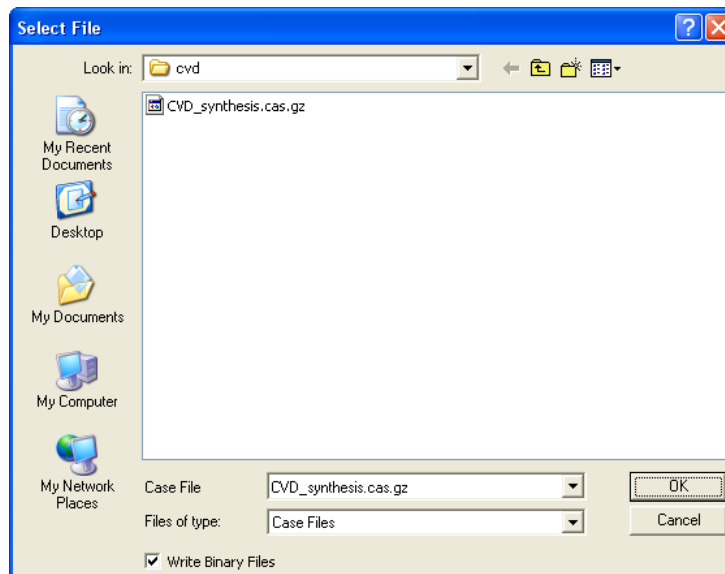
- (a) Select Plot in the Options list.
- (b) Click OK to close the Residual Monitors panel.

Note: By default, all variables will be monitored and checked for determining the convergence of the solution.

4. Save the case file, CVD_synthesis.cas.gz.

File → **Write** → Case...

Retain the default Write Binary Files on so that a binary file will be written.



- (a) Enter CVD_synthesis.cas.gz for Case File.
- (b) Click OK to close the Select File panel.

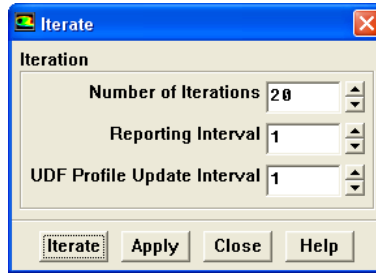
To monitor the convergence of the solution, we enable the plotting of H_2 mass fraction at the outlet (outlet). Iterate until this mass fraction has converged in order to ensure that the overall solution has converged. For the first few iterations of the calculation, when the solution is fluctuating, the values of this H_2 mass fraction will behave erratically. This can cause the scale of the y axis for the plot to be set too wide, and this will make variations in the value of the coefficients less evident. To avoid this problem, you will perform a small number of iterations and then set up the monitors.

Since, the H_2 mass fraction is a global variable indicating certain overall conditions; it may converge while conditions at specific points are still varying from one iteration to the next. To monitor this, you will create a point monitor at a point where there is likely to be significant variation, such as just downstream the furnace, and monitor the value of the CH_4 mass fraction.

After setting up the monitors, you will continue the calculation.

5. Start the calculation by requesting 20 iterations.

Solve → Iterate...

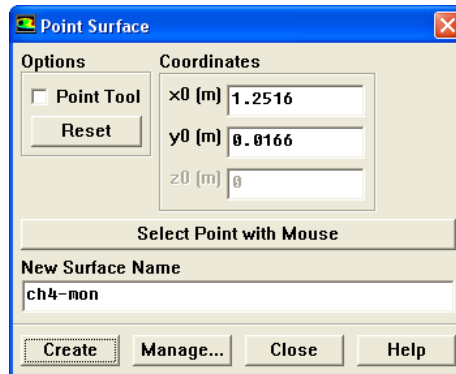


- (a) Enter 20 for the Number of Iterations.
- (b) Click Iterate.
- (c) Close the Iterate panel after completion of iterations.

This will be sufficient to achieve reduced convergence coefficient fluctuations.

- 6. Create a point surface to monitor the ch4 mass fraction.

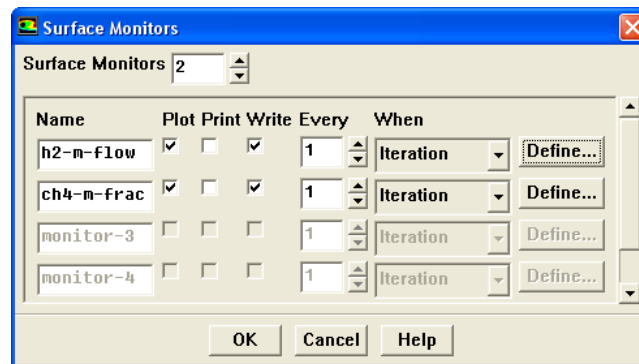
Surface → Point...



- (a) Enter 1.2516 m for x0 and 0.0166 m for y0 in the Coordinates group box.
- (b) Enter ch4-mon for the New Surface Name.
- (c) Click Create and close the Point Surface panel.

- 7. Define the surface monitors.

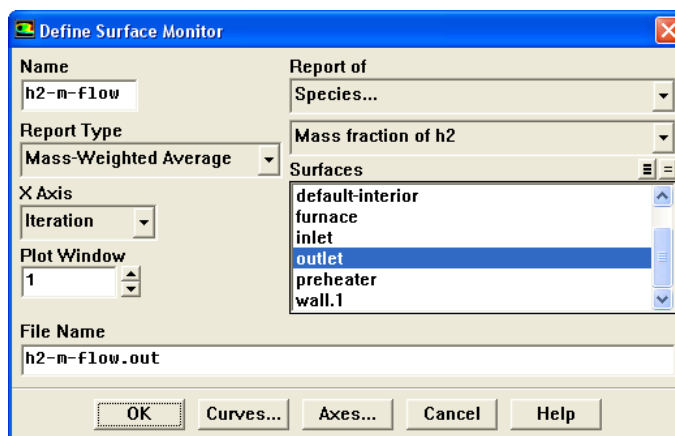
Solve → Monitors → Surface...



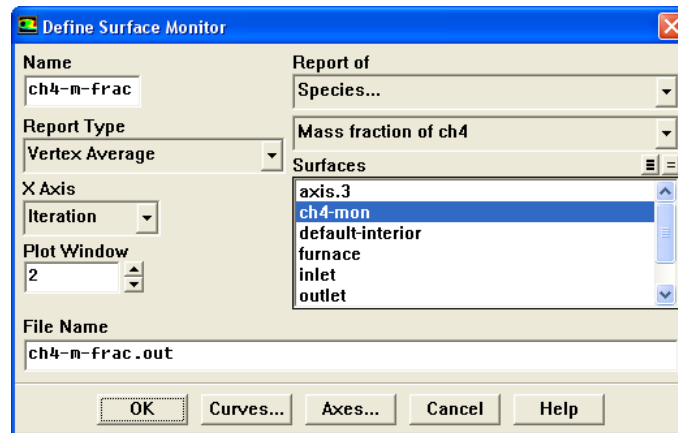
- (a) Set the Surface Monitors to 2.
- (b) Enable Plot and Write for the first monitor.
- (c) Enter `h2-m-flow` for the first monitor and `ch4-m-frac` for the second monitor as the Name.

When the Write option is enabled, the mass-averaged h2 mass fraction history is written to a file. If you do not select the Write option, the history information will be lost when you exit FLUENT .

- (d) Select Iteration from the When drop-down lists for both monitors.
- (e) Click Define... to define the first monitor.



- i. Select Mass-Weighted Average from the Report Type drop-down list.
 - ii. Select Iteration from the X Axis drop-down list.
 - iii. Select Species... and Mass fraction of h2 from the Report of drop-down lists.
 - iv. Select Outlet in the Surfaces list.
 - v. Enter `h2-m-flow.out` for the File Name.
 - vi. Click OK to close the Define Surface Monitor panel.
- (f) Click Define... to define the second monitor.



- i. Select Vertex Average from the Report Type drop-down list.
 - ii. Select Iteration from the X Axis drop-down list.
 - iii. Select Species... and Mass fraction of ch4 from the Report of drop-down lists.
 - iv. Select only ch4-mon in the Surfaces list.
 - v. Enter ch4-m-frac.out for the File Name.
 - vi. Click OK to close the Define Surface Monitor panel.
- (g) Click OK to close the Surface Monitors panel.
8. Start the calculation by requesting 1000 iterations.

Solve → Iterate...

Note: After about 595 iterations, the residual criteria are satisfied and FLUENT stops iterating. Save the case and data file as CVD_synthesis_first_order.cas.gz and CVD_synthesis_first_order.dat.gz. The CH₄ mass fraction, and H₂ mass fraction monitors indicates that the parameters are close to converge (Figure 13.3 and Figure 13.4). However, you have to run the solution for few more iterations to make sure that the H₂ and CH₄ mass fractions are converged.

The solution will generally converge faster for larger under-relaxation factors, unless the integration scheme becomes unstable. Since, you have performed some initial iteration, and the solution is stable, you may try increasing the under-relaxation factors to speed up the convergence. If the residuals start increasing without bound, or a floating point exception error occurs, you will need to decrease the under-relaxation factors, read in the previous data file, and try again.

Note: The number of iterations required for convergence varies according to the platform used. Also, since the residual values are different for different computers, the plot that appears on your screen may not be exactly the same as the one shown here.

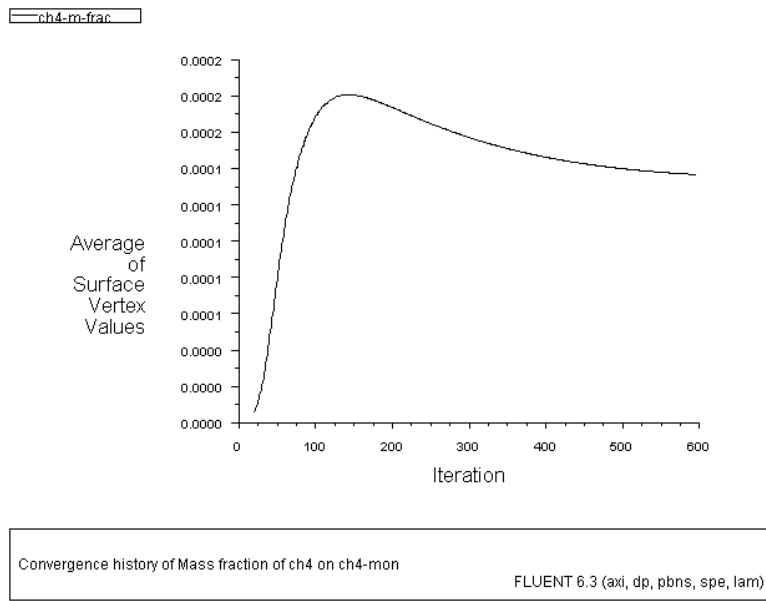


Figure 13.3: ch4 Convergence History for the Initial Calculation

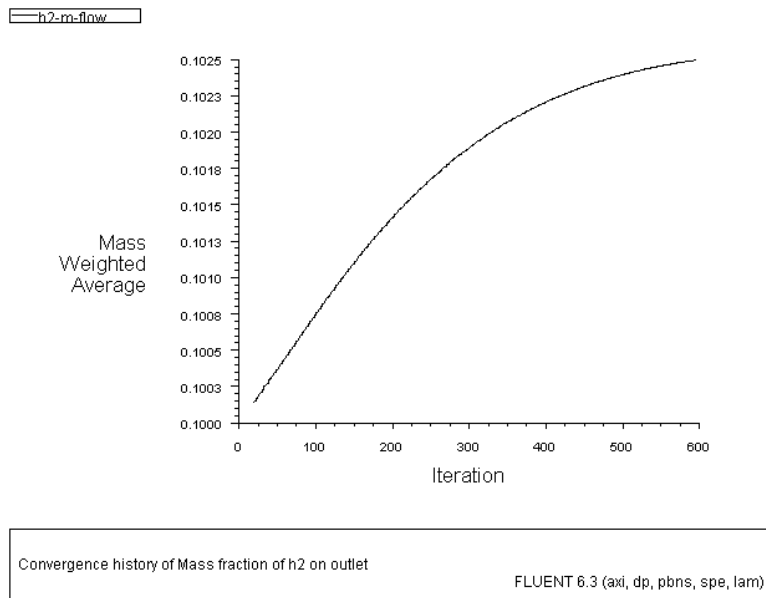
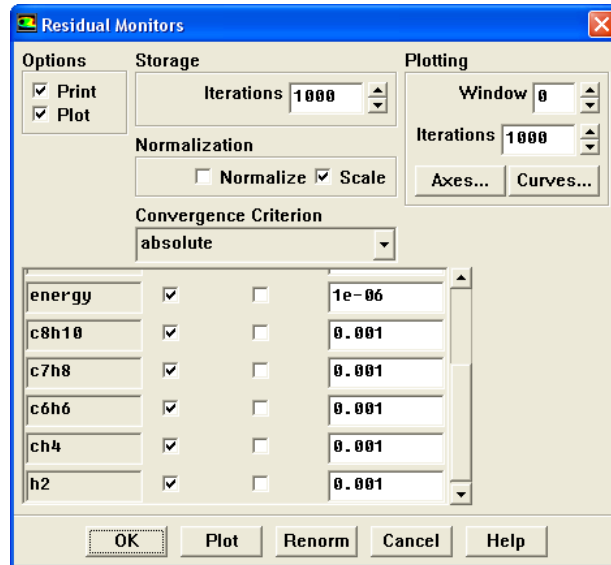


Figure 13.4: h2 Convergence History for the Initial Calculation

9. Start the calculations.

(a) Plot the residuals.

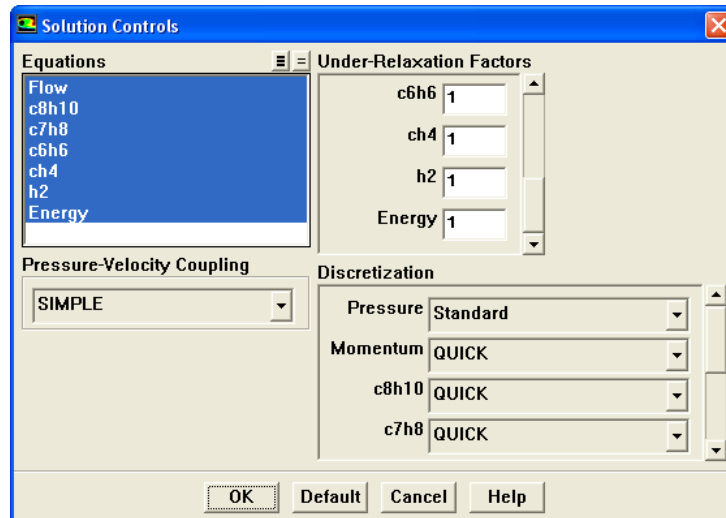
Solve → Monitors → Residual...



- i. Disable the Check Convergence for all the equations.
- ii. Click OK to close the Residual Monitors panel.

(b) Set the solution parameters.

Solve → Controls → Solution...



- i. Enter 0.7 for Momentum and 1 for Energy in the Under-Relaxation Factors group box.
- ii. Select QUICK for all the equations except Pressure in the Discretization group box.

- iii. Click OK to close the Solution Controls panel.
- (c) Continue the calculation by requesting 250 iterations.

Solve → Iterate...

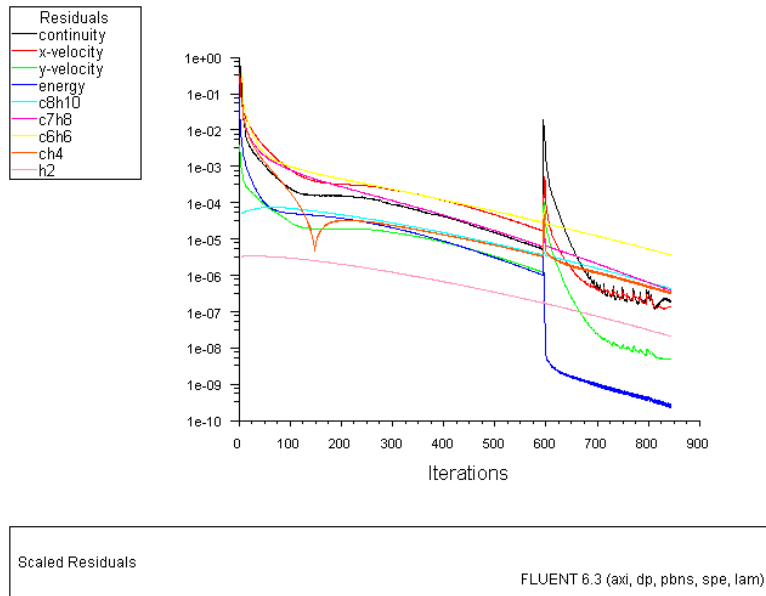


Figure 13.5: Residual Plots

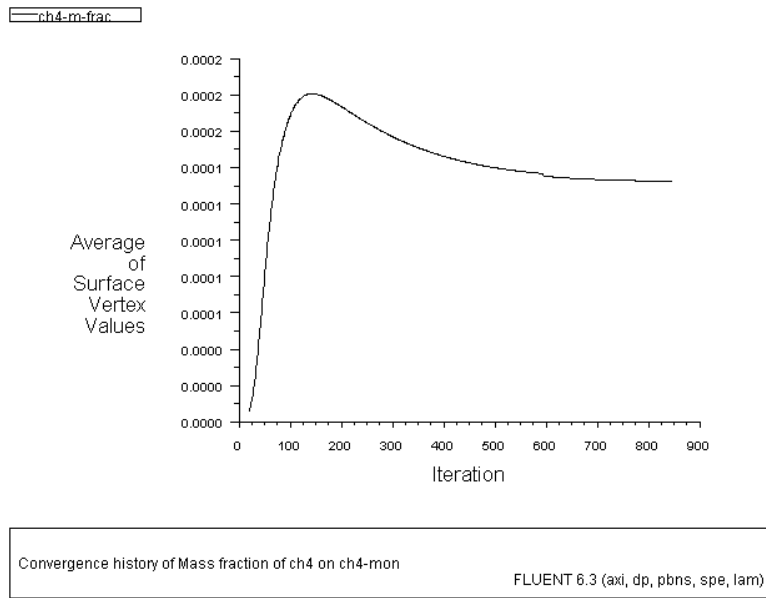


Figure 13.6: ch4 Convergence History

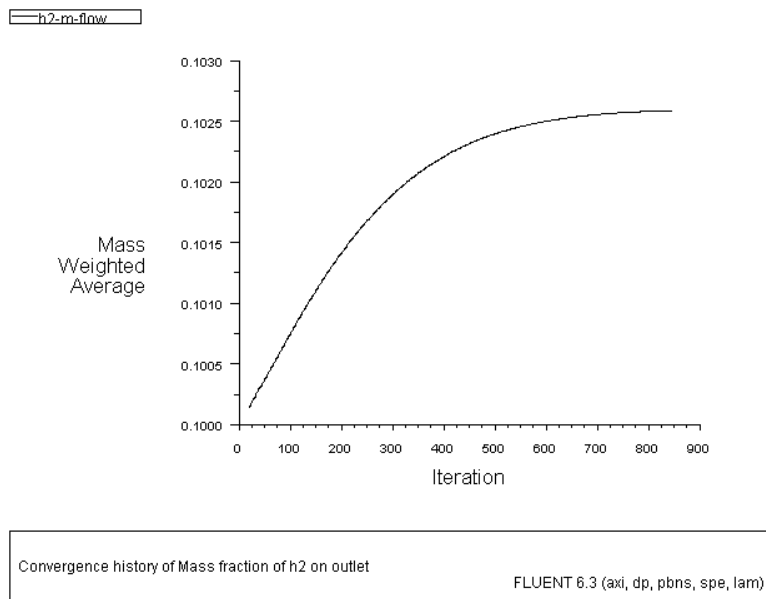
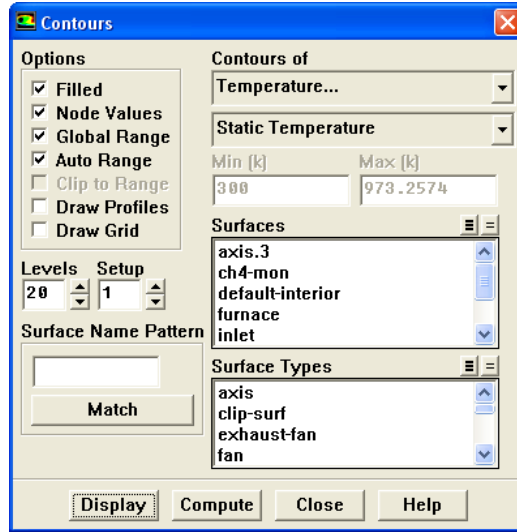


Figure 13.7: h2 Convergence History

Step 7: Post processing

1. Display filled contours of Temperature (Figure 13.8).

Display → Contours...



- (a) Select Temperature... and Static Temperature from the Contours of drop-down lists.
- (b) Select Filled in the Options list.
- (c) Click Display.

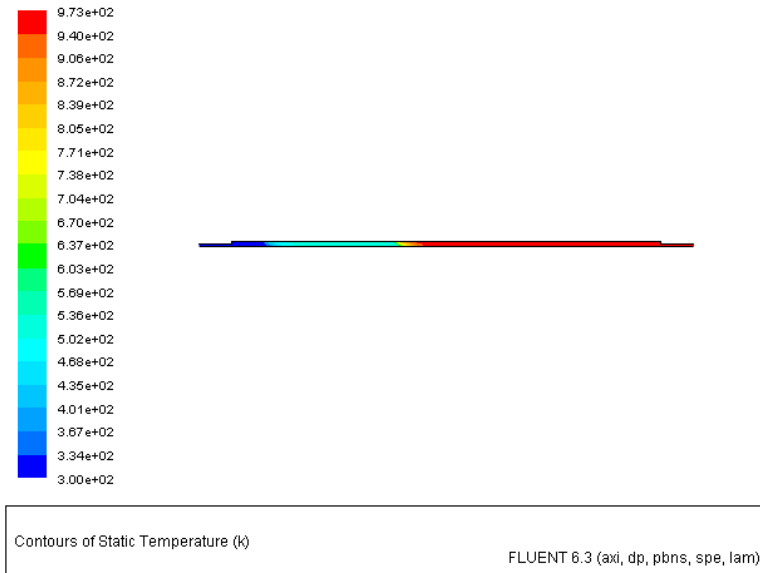
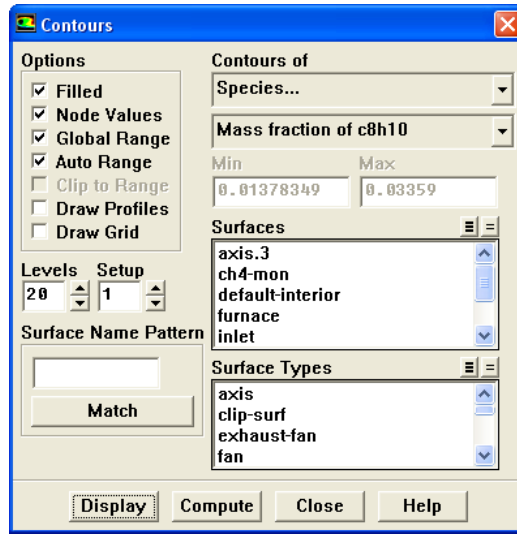


Figure 13.8: Predicted Static Temperature Distribution.

2. Display filled contours of c8h10 mass fraction (Figure 13.9).



- (a) Select Species... and Mass fraction of c8h10 from the Contours of drop-down lists.
- (b) Click Display and close the Contours panel.

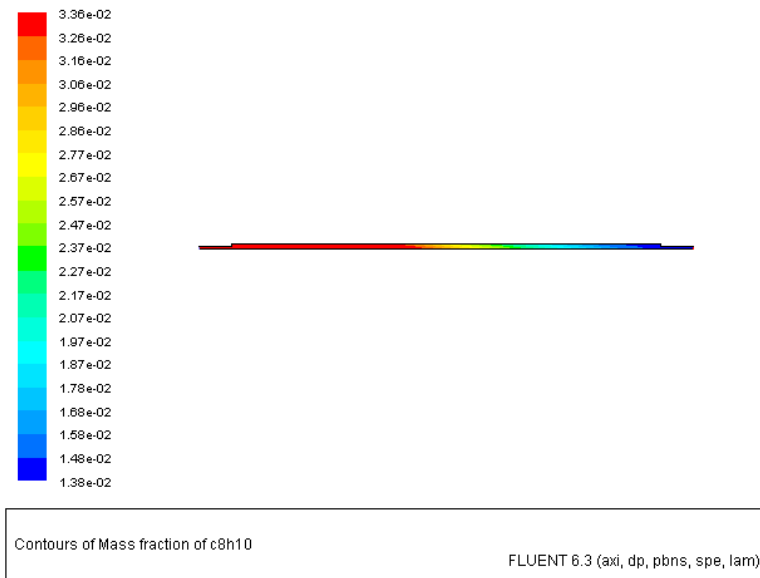
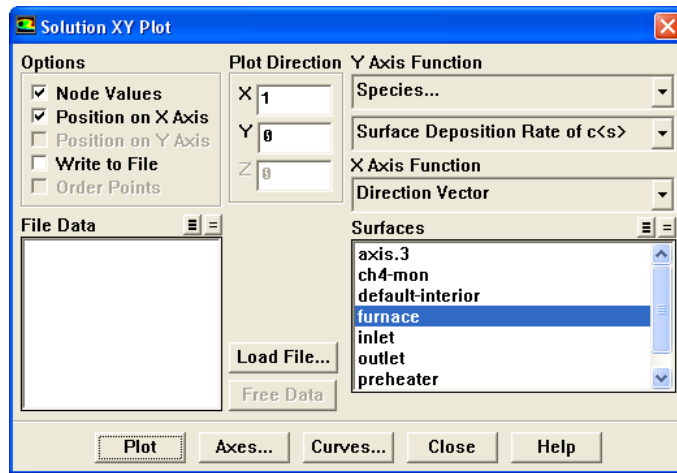


Figure 13.9: Predicted c8h10 Mass Fraction Distribution.

3. Plot the surface deposition rate of $c < s >$ distribution (Figure 13.10).

Plot → XY Plot...



- (a) Select Species... and Surface Deposition Rate of $c < s >$ from the Y Axis Function drop-down lists.
- (b) Select furnace from the Surfaces list.
- (c) Click Plot and close the Solution XY Plot panel.

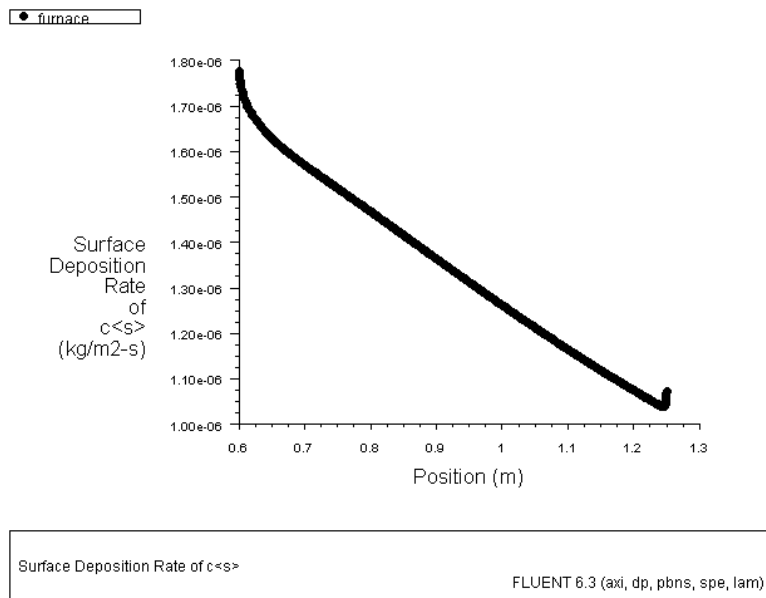
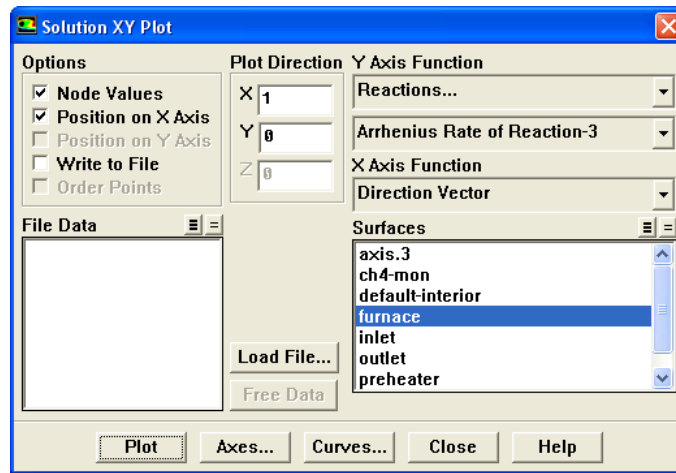


Figure 13.10: Predicted Surface Deposition Rate of $c < s >$ along the furnace.

- 4. Plot the arrhenius rate of reaction-3 distribution (Figure 13.11).

Plot → XY Plot...



- (a) Select Reactions... and Arrhenius Rate of Reaction-3 from the Y Axis Function drop-down lists.
- (b) Select furnace from the Surfaces list.
- (c) Click Plot and close the Solution XY Plot panel.

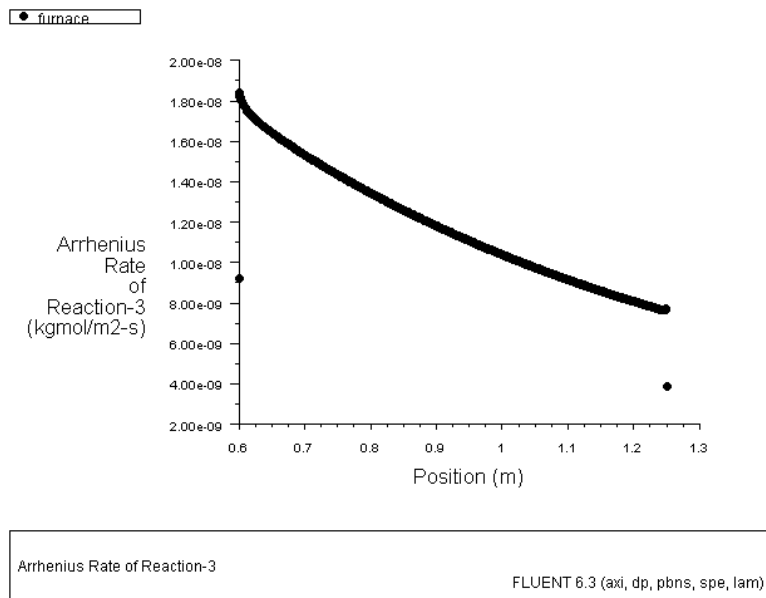


Figure 13.11: Predicted Arrhenius Rate of Reaction-3 Distribution.

Summary

In this tutorial, surface and volumetric reaction capabilities of FLUENT are illustrated for CVD synthesis of carbon nanotubes.

References

1. Endo H, Kuwana K, Saito K, Qian D, Andrews R, Grulke E A. CFD prediction of carbon nanotube production rate in a CVD reactor. Chem Phys Lett 2004:387:307-11.
2. FLUENT 6.3 User's Guide:
http://www.fluentusers.com/fluent6326/doc/ori/html/ug/main_pre.htm

Exercises/ Discussions

1. What will be the effect on surface deposition rate if thermo-physical properties of each species are temperature dependant?
2. What will be the effect on surface deposition rate if the catalyst preparation step, i.e. production of Fe particles on the furnace wall, is considered?

Links for Further Reading

- http://en.wikipedia.org/wiki/Carbon_nanotube
- <http://www.pa.msu.edu/cmp/csc/nanotube.html>