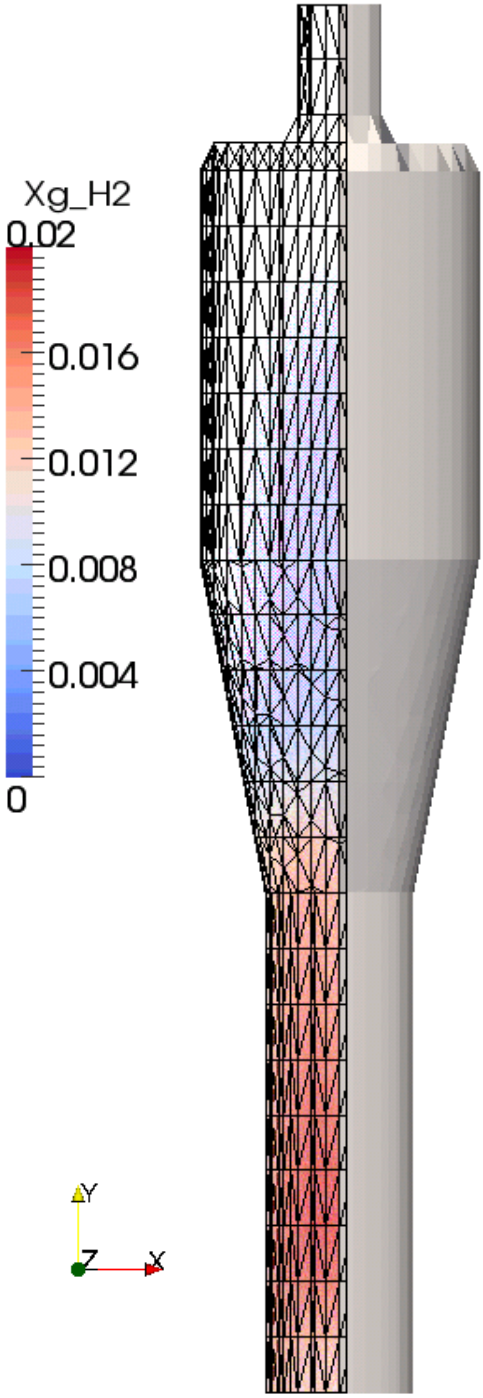
Tutorial: Silane Pyrolysis

This tutorial covers the model of a silane pyrolysis reaction vessel [1]. A mixture of silane (SiH_4) and nitrogen (N_2) are introduced though a uniform plate distributer and gas exits though a tube in the center top plate. Two reversible, homogeneous reactions and two heterogeneous decomposition reactions are considered. Results of similar simulations conducted with MFIX are available in [2].

General simulation overview:

- one solids phase
  - diameter, 82μm
  - density, 3.90 g/cm^3
  - composition: alumina (Al_2O_3) and silicon (Si)
- gas properties:
  - compressible
  - composition: silane (SiH_4), silylene (SiH_2), hydrogen (H_2), disilane (Si_2H_6), and nitrogen (N_2)
- gas inlet:
  - velocity, 7.89 cm/sec
  - temperature, 882.45K
  - pressure: 1 atm
  - composition (by mass):
    - 15.73% SiH_4
    - 84.27% N_2
- pressure outlet
  - pressure: 1 atm
  - temperature 882.45K
- operating pressure: 1 atm
- chemical reactions
  - employs stiff chemistry solver
  - $SiH_4 \leftrightarrow SiH_2 + H_2$ (homogeneous/reversible)
  - $SiH_6 \leftrightarrow SiH_2 + SiH_4$ (homogeneous/reversible)
  - $SiH_4 \longrightarrow Si + 2H_2$ (heterogeneous)
  - $SiH_2 \longrightarrow Si + H_2$ (heterogeneous)
- geometry
  - 10cm width, 50cm height, 10cm depth
  - 3D Cartesian grid cut-cell
    - 3460 standard computational cells
    - 1792 cut cells
    - 4748 blocked cells



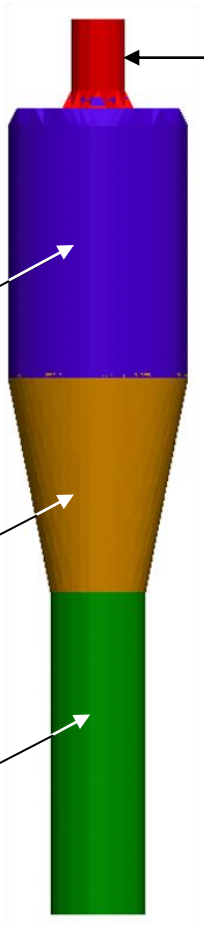
Geometry specification (mfix.dat):

The base domain decomposition is specified as 20 partitions in the x-axial direction, 25 partitions in the y-axial direction, and 20 partitions in the z-axial direction to a total background mesh of 10,000 cells. The resulting cell dimensions are 0.5cm x 2cm x 0.5cm in width, height, and depth, respectively.

```
COORDINATES = 'cartesian'

XLENGTH = 10.0    IMAX = 20   ! Width
ZLENGTH = 10.0    KMAX = 20   ! Depth
YLENGTH = 50.0    JMAX = 25   ! Height
```

The reactor geometry is specified using four quadratics: three cylinders and a cylinder-to-cylinder connector. The quadratics are placed into two groups; The first group specifies the main reactor geometry with two cylinders and the cylinder-to-cylinder connector. The second group is used to incorporate the pressure outlet.

```
GROUP_RELATION(1) = 'PIECEWISE'

  GROUP_SIZE(1) = 3
  GROUP_Q(1,1)  = 1
  GROUP_Q(1,2)  = 2
  GROUP_Q(1,3)  = 3

  QUADRIC_FORM(3)= 'Y_CYL_INT'
  RADIUS(3)      =    5.00
  t_x(3)         =    5.00
  t_z(3)         =    5.00

  PIECE_YMIN(3)  =   30.00
  CLIP_YMAX(3)   =   45.00
  BC_ID_Q(1)     =   15

  QUADRIC_FORM(2)=   'C2C'
  RADIUS(2)      =    0.0
  t_x(2)         =   -2.65
  t_z(2)         =   -2.65

  PIECE_YMIN(2)  =   -1.0
  BC_ID_Q(2)     =   15

  QUADRIC_FORM(1)= 'Y_CYL_INT'
  RADIUS(1)      =    2.65
  t_x(1)         =    5.00
  t_z(1)         =    5.00

  PIECE_YMAX(1)  =   18.00
  BC_ID_Q(1)     =   10
```



```
  GROUP_SIZE(2) = 1
  GROUP_Q(2,1)  = 4

  QUADRIC_FORM(4)= 'Y_CYL_INT'
  RADIUS(4)      =    1.50
  t_x(4)         =    5.00
  t_z(4)         =    5.00

  BC_ID_Q(4)     =   15
```

Phase composition specification (mfix.dat):

The gas phase is comprised of five species, `NMAX_g = 5`. The thermo-chemical database name and an alias are given for each species.

```
  SPECIES_g(1) = 'SiH4  Silane'     SPECIES_ALIAS_g(1) = 'SiH4'
  SPECIES_g(2) = 'SiH2  Silylene'   SPECIES_ALIAS_g(2) = 'SiH2'
  SPECIES_g(3) = 'H2 REF ELEMENT'   SPECIES_ALIAS_g(3) = 'H2'
  SPECIES_g(4) = 'SI2H6  Disilane'  SPECIES_ALIAS_g(4) = 'Si2H6'
  SPECIES_g(5) = 'N2'               SPECIES_ALIAS_g(5) = 'N2
```

Silylene, SiH_2, is not contained in the thermo-chemical database, therefore this information is appended to the end of the mfix.dat file. See the code Readme on the specific unit and formatting instructions.

```
#_____________________________________________________________________
THERMO DATA

SiH2  Silylene      91SI 1.H  4.  0.  0.G  200.000  6000.000  B  30.10140 1
 4.7354460E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00    2
 0.0000000E+00 0.0000000E+00 4.7354460E+00 0.0000000E+00 0.0000000E+00    3
 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 3.2810253E+04    4
```

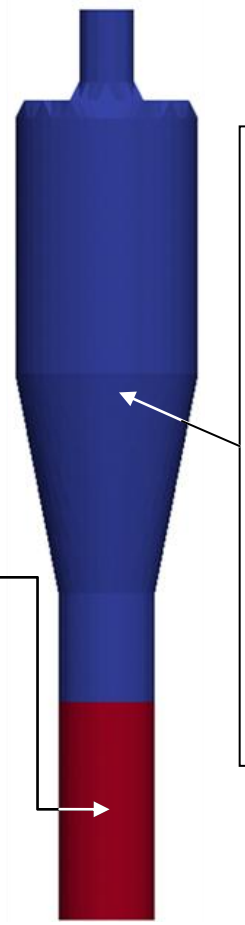
The solids phase composition is defined similarly.

```
  NMAX_s(1)      = 2
  SPECIES_s(1,1) = 'Si'       SPECIES_ALIAS_s(1,1) = 'Si'
  SPECIES_s(1,2) = 'AL2O3'    SPECIES_ALIAS_s(1,2) = 'Inert'
```

Initial condition specification (mfix.dat):

This simulation contains two sets of initial conditions. The first set of initial conditions for this simulation give the properties of the bed. The second set of initial conditions supplies the properties for the freeboard region. Note that the initial conditions for the bed contain quantities for the gas and solids whereas only gas phase quantities need be given for the freeboard region.

```
! Bed

IC_X_w(1) =      0.0     ! (cm)
IC_X_e(1) =     10.0     ! (cm)
IC_Z_b(1) =      0.0     ! (cm)
IC_Z_t(1) =     10.0     ! (cm)

IC_Y_s(1) =      0.0     ! (cm)
IC_Y_n(1) =     12.0     ! (cm)

IC_EP_g(1) =     0.5246 ! (-)
IC_P_Star(1) =   0.0     ! (dyne/cm^2)

IC_T_g(1)   =  882.45    ! (K)
IC_T_s(1,1) =  882.45    ! (K)

IC_U_g(1) =     0.00     ! (cm/sec)
IC_V_g(1) =     15.04    ! (cm/sec)
IC_W_g(1) =      0.00    ! (cm/sec)

IC_X_g(1,1) =    0.00    ! SiH4
IC_X_g(1,2) =    0.00    ! SiH2
IC_X_g(1,3) =    0.00    ! H2
IC_X_g(1,4) =    0.00    ! Si2H6
IC_X_g(1,5) =    1.00    ! N2

IC_U_s(1,1)  =   0.0     ! (cm/sec)
IC_V_s(1,1)  =   0.0     ! (cm/sec)
IC_W_s(1,1)  =   0.0     ! (cm/sec)

IC_X_s(1,1,1) =  0.0     ! Si
IC_X_s(1,1,2) =  1.0     ! Al2O3
```



```
! Freeboard

IC_X_w(2) =      0.0      ! (cm)
IC_X_e(2) =     10.0      ! (cm)
IC_Z_b(2) =      0.0      ! (cm)
IC_Z_t(2) =     10.0      ! (cm)

IC_Y_s(2) =     12.0      ! (cm)
IC_Y_n(2) =     50.0      ! (cm)

IC_EP_g(2) =     1.0      ! (-)
IC_P_Star(2) =   0.0      ! (dyne/cm^2)

IC_T_g(2) =    882.45     ! (K)
IC_T_s(2,1) =  882.45     ! (K)

IC_U_g(2) =     0.00      ! (cm/sec)
IC_V_g(2) =     7.89      ! (cm/sec)
IC_W_g(2) =     0.00      ! (cm/sec)

IC_X_g(2,1) =   0.00      ! SiH4
IC_X_g(2,2) =   0.00      ! SiH2
IC_X_g(2,3) =   0.00      ! H2
IC_X_g(2,4) =   0.00      ! Si2H6
IC_X_g(2,5) =   1.00      ! N2
```

Boundary condition specification (mfix.dat):

This simulation contains four boundary conditions. The location and dimensions of the flow boundaries are given explicitly. Conversely, wall boundary conditions are assigned to the reactor walls (i.e., cut cell surfaces) through the corresponding BC_ID of the cut-cell quadratics.

```
! Pressure Outlet

BC_X_w(2) =     0.0      ! (cm)
BC_X_e(2) =    10.0      ! (cm)
BC_Z_b(2) =     0.0      ! (cm)
BC_Z_t(2) =    10.0      ! (cm)

BC_Y_s(2) =    50.0      ! (cm)
BC_Y_n(2) =    50.0      ! (cm)

BC_TYPE(2) =    'PO'

BC_P_g(2) =     1.01d6   ! (dyne/cm^2)
BC_T_g(2) =   882.45     ! (K)
BC_T_s(2,1) = 882.45     ! (K)
```

```
! Gas Inlet

BC_X_w(1) =    0.0      ! (cm)
BC_X_e(1) =   10.0      ! (cm)
BC_Z_b(1) =    0.0      ! (cm)
BC_Z_t(1) =   10.0      ! (cm)

BC_Y_s(1) =    0.0      ! (cm)
BC_Y_n(1) =    0.0      ! (cm)

BC_TYPE(1) =   'MI'

BC_EP_g(1) =   1.0      ! (-)

BC_P_g(1) =    1.01d6   ! (dyne/cm^2)
BC_T_g(1) =  882.45     ! (K)

BC_U_g(1) =    0.00     ! (cm/sec)
BC_V_g(1) =    7.89     ! (cm/sec)
BC_W_g(1) =    0.00     ! (cm/sec)

BC_X_g(1,1) = 0.1573    ! SiH4
BC_X_g(1,2) = 0.00      ! SiH2
BC_X_g(1,3) = 0.00      ! H2
BC_X_g(1,4) = 0.00      ! Si2H6
BC_X_g(1,5) = 0.8427    ! N2
```

```
! Adiabatic Walls

BC_TYPE(15)    = 'CG_NSW'

BC_Hw_T_g(15)    = 0.0
BC_C_T_g(15)    = 0.0

BC_C_X_g(15,1) = 0.0
BC_C_X_g(15,2) = 0.0
BC_C_X_g(15,3) = 0.0
BC_C_X_g(15,4) = 0.0
BC_C_X_g(15,5) = 0.0
BC_Hw_X_g(15,1) = 0.0
BC_Hw_X_g(15,2) = 0.0
BC_Hw_X_g(15,3) = 0.0
BC_Hw_X_g(15,4) = 0.0
BC_Hw_X_g(15,5) = 0.0

BC_Hw_T_s(15,1)    = 0.0
BC_C_T_s(15,1)    = 0.0

BC_Hw_X_s(15,1,1) = 0.0
BC_Hw_X_s(15,1,2) = 0.0
BC_C_X_s(15,1,1) = 0.0
BC_C_X_s(15,1,2) = 0.0
```

```
! Constant Temperature Walls

BC_TYPE(10)    = 'CG_NSW'

BC_Tw_g(10)    = 882.45  ! (K)
BC_Tw_s(10,1) = 882.45  ! (K)

BC_C_X_g(10,1) = 0.0
BC_C_X_g(10,2) = 0.0
BC_C_X_g(10,3) = 0.0
BC_C_X_g(10,4) = 0.0
BC_C_X_g(10,5) = 0.0

BC_Hw_X_g(10,1) = 0.0
BC_Hw_X_g(10,2) = 0.0
BC_Hw_X_g(10,3) = 0.0
BC_Hw_X_g(10,4) = 0.0
BC_Hw_X_g(10,5) = 0.0

BC_Hw_X_s(10,1,1) = 0.0
BC_Hw_X_s(10,1,2) = 0.0
BC_C_X_s(10,1,1) = 0.0
BC_C_X_s(10,1,2) = 0.0
```

Chemical reaction specification (mfix.dat):

Chemical reactions are specified in the data file using the species aliases.

```
STIFF_CHEMISTRY = .T.

@(RXNS)

  RX1F { chem_eq = "SiH4 --> SiH2 + H2"}
  RX1R { chem_eq = "SiH2 + H2 --> SiH4"}

  RX2F { chem_eq = "Si2H6 --> SiH4 + SiH2"}
  RX2R { chem_eq = "SiH4 + SiH2 --> Si2H6"}

  RX3  { chem_eq = "SiH4 --> Si + 2H2"}

  RX4  { chem_eq = "SiH2 --> Si + H2"}

@(END)
```

The first line invokes the use of the stiff chemistry solver for these reactions. This removes sources terms arising from chemical reactions from the convection/diffusion transport equations and uses an ODE solver to apply chemical reactions at the end of each time step. **Note that this case will not run without using the stiff chemistry solver.**

The reaction block contains six reaction constructs. The first two constructs define the forward and reverse homogeneous reactions of silane decomposition. Likewise, the third and forth constructs give the forward and reverse homogeneous reactions for disilane decomposition. The last two constructs give the irreversible heterogeneous reactions for silicon deposition.

The reaction rates for all six reactions are provided in the `usr_rates.f` file. Reaction rates are given in g-mol/sec/cm^3 for CGS units and kg-mol/sec/m^3 for SI. The calculated rates are assigned to the `RATES` array. The array locatin for a given reaction is identified by the reaction construct name, (e.g., `RATES(RX1F)`).

Additional information on specifying chemical reactions is provided in Chemical Reaction section of the MFIX Readme.

References:

[1] B. Caussat, M. Hemati, J. Couderc, 1995, 'Silicon deposition from silane or disilane in a fluidized bed part 1: experimental study,' Chem. Engen. Sci, 43, 2037-2042.

[2] C. Guenther, T. O'Brien, and M. Syamlal, 2001, 'A numerical model of silane pyrolysis in a gas-solids fluidized bed.' Conference on Multiphase Flow, New Orleans, Louisiana.