



Approximations for a Cylindrical Flow CVD Reactor

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Summary

This application note explores three ways of modeling steady-state CVD in a cylindrical flow reactor, and compares the results of the levels of approximation.

Project Description

The three approximations are, in order of increasing simplification, Cylindrical Shear-layer Flow Reactor, Plug Flow Reactor, and a series of Perfectly Stirred Reactors.

The chemistry set used in this application describes the deposition of silicon nitride (Si_3N_4) from a mixture of SiF_4 and NH_3 .¹ This mechanism demonstrates one way of describing the deposition of a compound solid, but it should generally be considered as illustrative only and not as a source of kinetic data for Si_3N_4 deposition.

The chemistry input file, *chem.inp*, includes 4 elements, 17 gas-phase species and 33 reactions. The first 27 of these reactions describe the pyrolysis of ammonia, and are taken from published models for ammonia oxidation and De-NOx.² The other six reactions describe SiF_4 decomposition and likely cross reactions between Si and N-containing species. Rate parameters were not available in the literature for these reactions, so the mechanism uses estimates based on bond strengths and analogies with related gas-phase reactions.

The surface chemistry file, *surf.inp*, defines six surface species in the Si_3N_4 surface phase and the Si_3N_4 solid, which is defined in terms of two bulk phases, Si(D) and N(D). The surface species all occupy more than one site, and have placeholder thermodynamic data. Six irreversible surface reactions are also defined in this file. The surface reactions are “lumped” reactions, meaning that they each represent several elementary steps that have been combined into one reaction. Rate parameters for these surface reactions were determined by fitting the model results to experimental deposition-rate data. The activation energies for the surface reactions are all zero, which reflects the limitations of the experimental data set used to derive the rate parameters. Although it is not immediately obvious, the surface species and reactions were designed to produce a bulk-phase stoichiometry of 3 Si to 4 N. The densities of bulk species has been defined to force the linear deposition rates of either Si(D) or N(D) to match the experimentally observed deposition rate for Si_3N_4 . These reactions have zero as activation

¹M. E. Coltrin, P. Ho, Sandia National Laboratories, private communication.

²J. A. Miller, M. D. Smooke, R. M. Green, and R. J. Kee, *Comb. Sci. Technol.* **34**:149 (1983).

energies because they were fit to an experimental data set taken at one temperature. These rates would therefore not be likely to be valid at other temperatures.

Project Setup

This project is an example of a project that contains multiple sub-projects. The first reactor diagram contains one inlet and a network of 10 sequential PSRs. The other two reactor diagrams in this project are simple ones that contain only one inlet and either a Plug Flow or a Cylindrical Shear-Flow Reactor Model.

Cylindrical Shear-Flow Reactor

Use the Stream Property Data tab of the R1_IN1 panel to input the inlet gas temperature and mass flow rate. The mass flow rate is the maximum gas-phase velocity at the inlet. For this application, which is in cylindrical coordinates, the average velocity equals one-half of the maximum velocity of the assumed parabolic velocity profile. On the Species-specific Property tab of the R1_IN1 panel, input the composition of the inlet gas. This application uses mole fraction, but you may choose to input these values in mass fractions instead.

Enter parameters describing the reactor geometry and wall temperature on the Reactor Physical Property tab of the C1_Cylindrical Shear Flow panel. The temperatures for the wall are input on this tab. In this case, the inlet gas temperature is equal to the wall temperature, so there is no need to provide transitioning parameters. You also enter the pressure, grid parameters, as well as the use of multicomponent diffusion and thermal diffusion (the Soret effect) on this tab. To be consistent in our approximation to the Plug Flow as well as to the multiple PSR examples, the Boundary Layer Thickness has been set to 0.01 cm, to provide an initially flat velocity profile. The Species-specific Data tab allows the specification of initial guesses for the gas composition adjacent to the surface, which is not used in this example, as well as estimated values for the surface site fractions and bulk activities, which are provided. Making a good initial guess for these values is very helpful in attaining convergence. The Output Control panel has been configured so that the text output file should have solution data printed every 1 cm.

Plug Flow Reactor

The properties of the inlet gas are described on the R1_IN1 panel. You can specify the inlet mass flow rate on the Stream Property Data tab and the composition of the inlet gas on the Species-specific Property tab of the R1_IN1 panel. This application uses mole fractions, but you may choose to input these values in mass fractions instead.

Go to the Reactor Physical Property tab of the C1_PFR panel to specify parameters describing the reactor geometry and gas temperature. The problem type and pressure are also specified on this tab. The Species-specific Data tab allows the specification of initial guesses for the surface site fractions

and bulk activities. On the Solver panel, the only value that needs attention is to specify that the text output file should have solution data printed every 1 cm.

Perfectly-stirred Reactor Network

As with the other sub-projects, you input the properties of the inlet gas for the series PSR project on the R1_IN1 panel. Go to the Stream Property Data tab to input the mass flow rate. Input the composition of the inlet gas on the Species-specific Property tab of the R1_IN1 panel.

This sub-project contains a series of 10 identical PSR reactors, so in this case, the C1_Rx PSR (where $x = 1 - 10$) panels have no entries. Instead, you input the properties of these reactors on the C1 Cluster Properties panel. Cluster properties will apply to all PSRs in the cluster unless overridden in the individual reactor panels. Parameters describing the problem type, reactor geometry, pressure, and gas temperature are entered on the Property for All Reactors tab of the Cluster Properties panel. The Species-specific Data for All Reactors tab allows you to specify initial guesses for the gas composition, which are not used in this example, as well as estimated values for the surface site fractions and bulk activities, which are used. A good initial guess for these values is very helpful in attaining convergence.

Project Results

Figure 1 shows a contour plot of the SiF_4 mole fractions as a function of radial and axial position in the shear flow simulation. There is a minor degree of radial non-uniformity for this reactant species, as a result of chemical reactions consuming SiF_4 at the wall. *Figure 2* shows SiF_4 mole fraction as a function of axial distance for all three simulations. The mole fraction for the centerline is higher than that for the upper-wall in the shear-flow simulation, as expected, and these results bracket the results from the plug-flow and series-PSR simulations. Although not shown, the area-averaged value for the SiF_4 mole fraction from the shear-flow simulation agrees well with the results from the other two simulations.

Figure 1 Cylindrical Channel Flow—Shear-flow Simulation of SiF₄ Mole Fractions

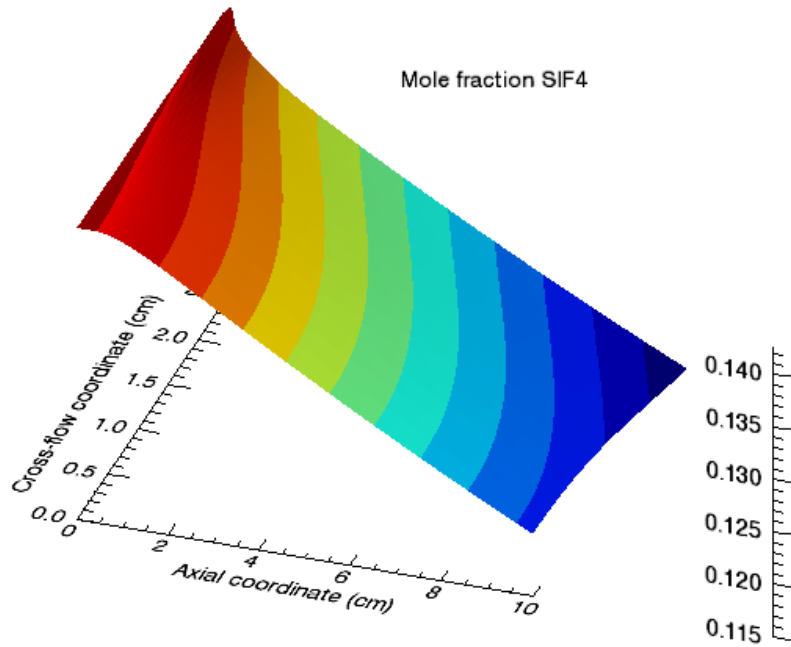


Figure 2 Cylindrical Channel Flow—SiF₄ Mole Fractions Comparison

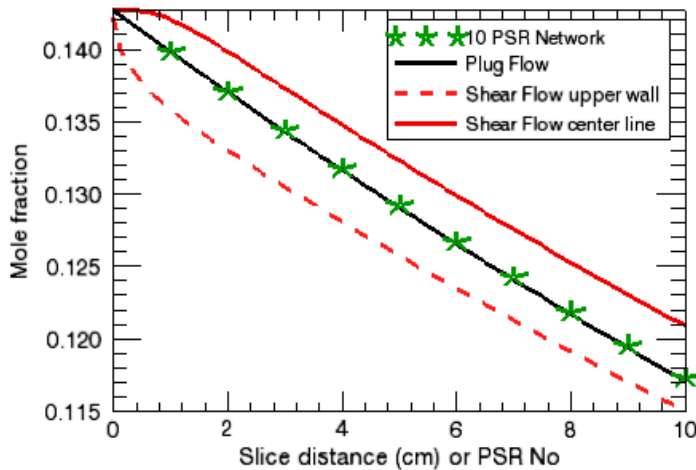


Figure 3 shows the silicon nitride deposition rates from these three simulations. The predictions from the plug-flow and series-PSR simulations are nearly identical, with the shear-flow simulations results being somewhat lower. Although there are some differences in the axial gas velocities shown in Figure 4 for the shear-flow and plug flow simulations, the difference in deposition rates mostly results from the lower reactant concentrations at the surface in the higher-dimensional simulations. The series of 10 PSR reactors and the Plug Flow simulations represent comparable levels of approximation to the channel flow. As the Plug Flow simulation actually runs faster, it would be the recommended reactor

model to use in developing chemical mechanisms, or for exploring general trends for these conditions. However, the series-PSR approach has the advantage that it can approximate transient flow, as well as steady-state flow, in a channel. The deposition rate is affected by mass-transfer in this case, so the higher-dimensionality shear-flow simulations would be used for final mechanism adjustment and reactor design simulations.

Figure 3 Cylindrical Channel Flow—Deposition Rates Comparison

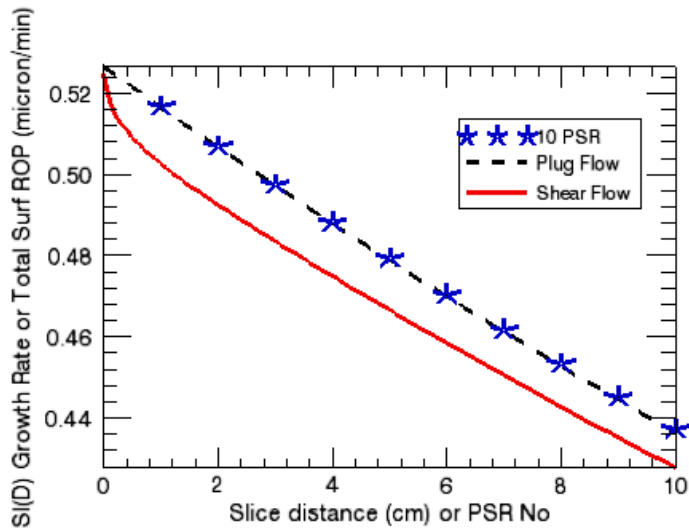
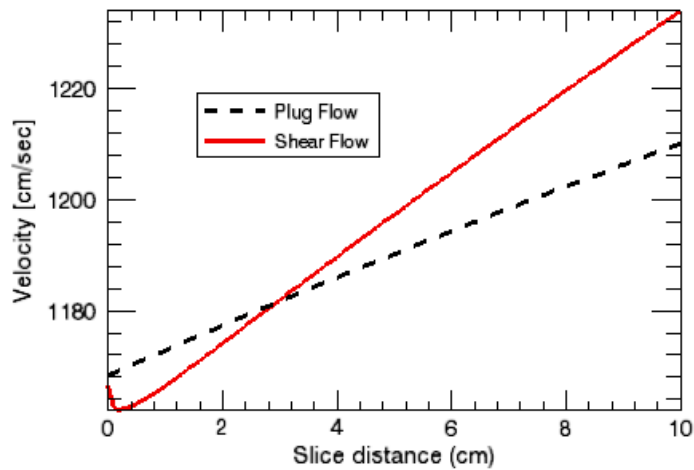


Figure 4 Cylindrical Channel Flow—Axial Gas Velocities Comparison



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