Modeling the Transient Behavior of Plug Flow Reactors

A Computer Project Applying
the Ability to Numerically Solve Engineering Problems
described by
Systems of Nonlinear Parabolic Partial Differential Equations

Advanced Engineering Mathematics
ChE 505
Department of Chemical Engineering
University of Tennessee
Knoxville, TN

Project Designed by
Dr. David Keffer
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I. Objective

The objective of this project is to describe a relevant engineering system modeled by a system of nonlinear parabolic partial differential equations. This description will require the solution of the system of equations using a numerical method. Finally, meaningful engineering insight will be drawn from the transient and steady-state solution of the equations and their response to a sensitivity analysis of physical parameters and process variables.

II. Derivation of PDEs

A plug flow reactor (PFR) is a pipe. Reactants are fed in one end of the pipe and some mixture of reactants and products emerge from the far end. The concentration of species and the temperature inside the PFR can vary with time (t), axial position (z), radial position (r), and angular position (θ). For the purposes of this derivation, we are going to assume that the variation in the radial and angular directions are negligible. Therefore, the concentrations and temperatures are only functions of time and axial position.

The equations that describe the behavior of a plug flow reactor are material and energy balances. As material and energy balances, they have the functional form:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} \tag{1}$$

We now write a differential mole balance on an arbitrary species A. The units of this equation are moles/time. The system over which the balance is performed is a cross-sectional disc with width Δz. The volume of this differential volume is

$$\Delta V = A_{cross}\Delta z = \frac{\pi D_R^2}{4}\Delta z \tag{2}$$

where D_R is the diameter of the pipe.

$$\text{accumulation} = \Delta V \frac{\partial C_A}{\partial t} \tag{3.a}$$

Moles of A can enter the system by convection.

$$\text{in by convection} = \left[vA_{cross}C_A\right]_z \tag{3.b}$$

where v is the bulk velocity in the axial direction at position z. Moles of A can leave the system by convection.

$$\text{out by convection} = \left[vA_{cross}C_A\right]_{z+\Delta z} \tag{3.c}$$

Moles of A can enter the system by diffusion down a concentration gradient.

$$\text{in by diffusion} = \left[A_{cross}J_A\right]_z \tag{3.d}$$

where J_A is the molar flux of species A in the axial direction at position z. Moles of A can leave the system by diffusion down a concentration gradient.

$$\text{out by diffusion} = \left[A_{cross} J_A\right]_{z+\Delta z} \tag{3.e}$$

Moles of A can be generated by a chemical reaction.

$$\text{generation} = \upsilon_A \Delta V \cdot \text{rate} \tag{3.f}$$

where rate is the rate of chemical reaction and υ_A is a stoichiometric coefficient for A in the reaction (negative for reactants and positive for products).

Next we combine terms (3.a) to (3.f) in a mass balance. We divide by the differential volume and take the limit as Δz goes to zero. This yields

$$\Delta V \frac{\partial C_A}{\partial t} = \left[v A_{cross} C_A\right]_z - \left[v A_{cross} C_A\right]_{z+\Delta z} + \left[A_{cross} J_A\right]_z - \left[A_{cross} J_A\right]_{z+\Delta z} + \upsilon_A \Delta V \cdot \text{rate}$$

$$\frac{\partial C_A}{\partial t} = -\frac{\partial (v C_A)}{\partial z} - \frac{\partial (J_A)}{\partial z} + \upsilon_A \cdot \text{rate} \tag{4}$$

Fick's law of diffusion relates the molar flux, J_A, to the concentration gradient

$$J_A = -D \frac{\partial C_A}{\partial z} \tag{5}$$

The rate of the reaction for an elementary irreversible reaction of the form:

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_C C + \upsilon_D D \tag{6}$$

is

$$\text{rate}_{forward} = k_f C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{7}$$

where the rate constant, k, is generally given as

$$k_f = k_{o,f} e^{-\frac{E_{a,f}}{RT}} \tag{8}$$

where R is the gas constant, T is the temperature, $E_{a,f}$ is the activation energy, and $k_{o,f}$ is the exponential prefactor. Remember, the rate has units of [moles/volume/time] so $k_{o,f}$ has variable units depending upon the stoichiometry of the reaction.

If the reaction is irreversible, then we can write the reverse rate as

$$\text{rate}_{\text{reverse}} = k_r C_C^{|\upsilon_C|} C_D^{|\upsilon_D|} \tag{9}$$

Substituting Fick's law and the forward and reverse rates into the material balance, we have

$$\frac{\partial C_A}{\partial t} = -\frac{\partial (v C_A)}{\partial z} + \frac{\partial}{\partial z}\left(D \frac{\partial C_A}{\partial z} \right) + \upsilon_A k_{o,f} e^{-\frac{E_{a,f}}{RT}} C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} - \upsilon_A k_{o,r} e^{-\frac{E_{a,r}}{RT}} C_C^{|\upsilon_C|} C_D^{|\upsilon_D|} \tag{10}$$

If the velocity and the diffusivity are assumed constant with respect to Temperature and concentration, then equation (10) can be simplified to give:

$$\frac{\partial C_A}{\partial t} = -v \frac{\partial (C_A)}{\partial z} + D \frac{\partial^2 C_A}{\partial z^2} + \upsilon_A k_{o,f} e^{-\frac{E_{a,f}}{RT}} C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} - \upsilon_A k_{o,r} e^{-\frac{E_{a,r}}{RT}} C_C^{|\upsilon_C|} C_D^{|\upsilon_D|} \tag{11}$$

Equations of this form can be written for every species in the reactor. For a non-reactive solvent species, the balance simplifies to

$$\frac{\partial C_S}{\partial t} = -v \frac{\partial (C_S)}{\partial z} + D \frac{\partial^2 C_S}{\partial z^2} \tag{12}$$

The energy balance for a plug flow reactor can be derived in an analogous manner. We again perform a balance over a differential element. However before we begin we are going to make a few assumptions about our system. The molar enthalpy of our system, $\tilde{H}$, is an ideal enthalpy defined as

$$\tilde{H} = \sum_{i=1}^{n_c} x_i \tilde{H}_i = \sum_{i=1}^{n_c} x_i C_{p,i} (T - T_{ref}) \qquad \left[\frac{\text{energy}}{\text{mole}} \right] \tag{13.a}$$

where T_{ref} is a thermodynamic reference temperature. (If you choose it to be 0 K, it disappears from the equation.) The heat capacity of species i is $C_{p,i}$. This is the pure component enthalpies weighted by mole fraction, x_i. Of course, it is inconvenient to use mole fractions, since we are working in concentrations. But the mole fraction can be obtained from

$$x_i = \frac{C_i}{\sum_{i=1}^{n_c} C_i} = \frac{C_i}{C_T} \tag{14}$$

where C_T is the total molar concentration. C_T is not necessarily constant but it frequently is assumed to be so. It turns out that we are going to want the enthalpy per volume, so we need to

convert the molar enthalpy to a volumetric enthalpy. This is done by multiplying by C_T. This gives a volumetric enthalpy of

$$H = \sum_{i=1}^{n_c} C_i C_{p,i}(T - T_{ref}) \quad \left[\frac{\text{energy}}{\text{volume}}\right] \tag{13.b}$$

Heat enters our differential volume in the same ways that mass does—namely by convection and diffusion. We will have analogous terms in our energy balance for these phenomena. The diffusion term will rely on Fourier's law rather than Fick's law to relate the heat flux to the temperature gradient, with the proportionality constant being, k_c, the thermal conductivity.

$$q = -k_c \frac{\partial T}{\partial z} \tag{15}$$

Also, heat can be generated or consumed by reaction. The molar heat of reaction is related to the activation energies as follows

$$\Delta H_r = E_{a,f} - E_{a,r} \tag{16}$$

Heat can also be lost through the reactor walls due to poor insulation or intentional cooling. Generally this heat loss has the form:

$$Q = A_{surf} h (T_{surr} - T) \tag{17}$$

where A_{surf} is the surface area, h is the heat transfer coefficient, and T_{surr} is the temperature of the surroundings.

Thus we can write an energy balance as

$$\frac{\partial H}{\partial t} = -v\frac{\partial H}{\partial z} + k_c \frac{\partial^2 T}{\partial z^2} - \Delta H_r k_{o,f} e^{-\frac{E_{a,f}}{RT}} C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} + \Delta H_r k_{o,r} e^{-\frac{E_{a,r}}{RT}} C_C^{|\upsilon_C|} C_D^{|\upsilon_D|} + \frac{A_{surf} h (T_{surr} - T)}{V_r} \tag{18}$$

where we have already divided by the reactor volume and taken the limit as Δz approaches zero.

The units of equation (18) (and thus the units of every term in this equation) are energy/volume/time. Now we need to substitute equation (13.b) in for the enthalpy so that we obtain a PDE which is given in terms of the temperature. In the following analysis we assume that the heat capacities are not functions of temperature.

$$\frac{\partial H}{\partial t} = \frac{\partial \sum_{i=1}^{n_c} C_i C_{p,i}(T - T_{ref})}{\partial t} = (T - T_{ref}) \sum_{i=1}^{n_c} C_{p,i} \frac{\partial C_i}{\partial t} + \frac{\partial T}{\partial t} \sum_{i=1}^{n_c} C_{p,i} C_i \tag{19}$$

Similarly, the spatial derivative of the enthalpy can be obtained.

$$\frac{\partial H}{\partial z} = \frac{\partial \sum_{i=1}^{n_c} C_i C_{p,i} (T - T_{ref})}{\partial z} = (T - T_{ref}) \sum_{i=1}^{n_c} C_{p,i} \frac{\partial C_i}{\partial z} + \frac{\partial T}{\partial z} \sum_{i=1}^{n_c} C_{p,i} C_i \tag{20}$$

Substituting equation (19) and (20) into equation (18) and rearranging for $\frac{\partial T}{\partial t}$ yields

$$\frac{\partial T}{\partial t} = \frac{\left\{ \begin{array}{l} -v\left[(T - T_{ref}) \sum_{i=1}^{n_c} C_{p,i} \frac{\partial C_i}{\partial z} + \frac{\partial T}{\partial z} \sum_{i=1}^{n_c} C_{p,i} C_i \right] + k_c \frac{\partial^2 T}{\partial z^2} - \Delta H_r k_{o,f} e^{-\frac{E_{a,f}}{RT}} C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \\ + \Delta H_r k_{o,r} e^{-\frac{E_{a,r}}{RT}} C_C^{|\upsilon_C|} C_D^{|\upsilon_D|} + \frac{A_{surf} h (T_{surr} - T)}{V_r} - (T - T_{ref}) \sum_{i=1}^{n_c} C_{p,i} \frac{\partial C_i}{\partial t} \end{array} \right\}}{\sum_{i=1}^{n_c} C_{p,i} C_i} \tag{21}$$

Thus we have our very wonderful energy balance. It happens to be a function of the temporal derivatives of the concentrations but as long as, at each step of the Runge-Kutta process, we solve the mass balance equations first, we will have the values needed to substitute into equation (21).

III. Problem Specifications

stoichiometry

$$\nu_A = -1 \qquad \nu_B = -1 \qquad \nu_C = 1 \qquad \nu_D = 0$$

Boundary conditions at entrance. (at z = 0)

$C_{A,1} = 1.0$ [moles/liter]
$C_{B,1} = 2.0$ [moles/liter]
$C_{C,1} = 0.0$ [moles/liter]
$C_{S,1} = C_T - C_{A,1} - C_{B,1} - C_{C,1}$ [moles/liter]
$T_1 = 300.0$ [K]

Boundary conditions at exit. (at z = L)

$$\frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x} = \frac{\partial C_C}{\partial x} = \frac{\partial C_S}{\partial x} = \frac{\partial T}{\partial x} = 0.0$$

Initial conditions inside reactor

$C_{A,o} = C_{B,o} = C_{C,o} = 0.0$
$C_{S,o} = C_T$
$T_o = 300.0$

parameters:

$C_T = \frac{1000}{18}$ [moles/liter] (total concentration)
$D_R = 0.01$ [m]
$L = 0.2$ [m]
$D = 1.0 \cdot 10^{-7}$ [m^2/sec]
$k_{o,f} = 5000.0$ [l/mol/sec]
$k_{o,r} = 5000.0$ [1/sec]
$E_{a,f} = 4 \cdot 10^4$ [Joules/mole]
$E_{a,r} = 8 \cdot 10^4$ [Joules/mole]
$R = 8.314$ [J/mole/K]
$k_c = 2.0 \cdot 10^{-4}$ [J/m/K/sec]
$h = 2.0 \cdot 10^{-4}$ [J/m^2/K/sec]
$MW = 0.0180$ [kg/mol]
$C_{p,water} = 4184.0$ [J/kg/K]

$C_{p,A} = 1.2C_{p,water}$ [J/kg/K]

$C_{p,B} = 1.3C_{p,water}$ [J/kg/K]

$C_{p,C} = 1.5C_{p,water}$ [J/kg/K]

$C_{p,S} = 1.0C_{p,water}$ [J/kg/K]

$T_{surr} = 273$ [K]

$\tau = 5000$ [sec] (residence time)

$v = \frac{L}{\tau}$ [m/sec] (velocity)

$A_{surf} = \pi D_R L$ [m^2] (surface area)

$V = \pi \frac{D_R^{\ 2}}{4} L$ [m^3] (reactor volume)

IV. Numerical Considerations

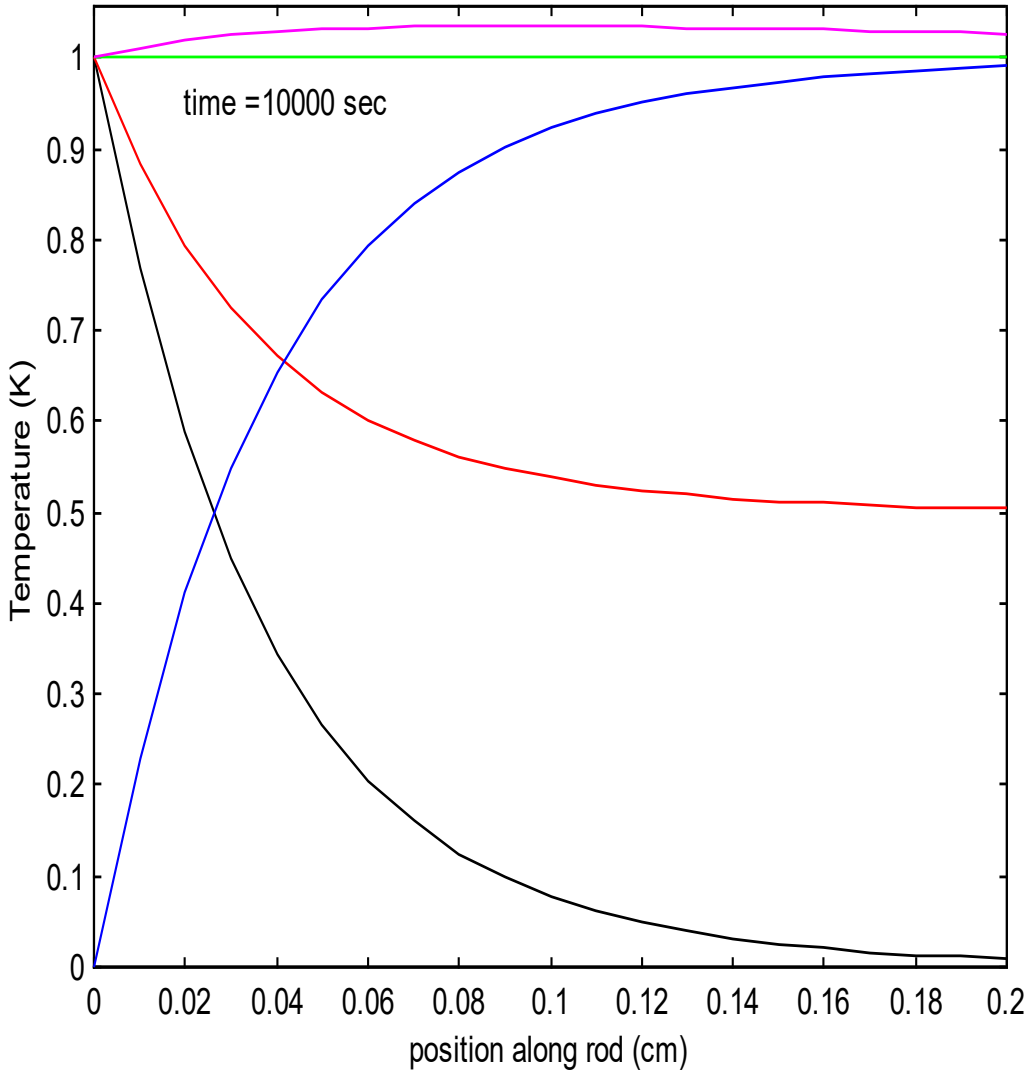
You will need to employ a numerical method capable of solving a system of coupled, nonlinear, parabolic partial differential equations with Dirichlet and Neumann boundary conditions.

The code syspde_para.m with the input file syspde_para_input.m are capable of performing this task. You will need to modify the initial conditions, boundary conditions, PDEs, and parameters to suit your particular problem.

V. Assignment

Task One.

For the parameters given above, solve the system of five PDEs. Use 20 spatial nodes and 1000 temporal nodes spanning from $t_o = 0$ to $t_f = 10{,}000$ sec. Check that you have the code working properly by examining the profiles of the concentrations and the temperatures at 10,000 sec. They should look something like the following graph, where black = A, red = B, blue = C, green = S, and magenta = T. In this plot, the concentrations of A, B, and S and the temperature have been normalized by their input values at z=0. The concentration of C has been normalized by the input value of the limiting reagent, A.



Task Two.

Select one of the physical parameters,

$$D\,,\ k_{o,f}\,,k_{o,r}\,,\ E_{a,f}\,,\ E_{a,r}\,,k_c\,,\ C_p\,,\ C_T\,,\ h\,,\ \text{or reaction stoichiometry}$$

Investigate how the reactor behavior changes as you change the variable. Discuss differences in both transient and steady-state behavior. Submit a plot which has on the x-axis the variable you are changing and on the y-axis the steady-state temperature and conversion. (Remember:

$$\text{conversion} = \frac{C_{A,in} - C_{A,out}(t = \text{steady state})}{C_{A,in}}$$

where A is the limiting reactant.) Vary the physical parameter over a range so that the effect of the parameter is visible from the graphs.

If the effect of the physical parameter is not visible given the other base case parameters, you may change those parameters. For example, if the effect of changing the diffusivity is not visible because the reactor is dominated by convection, you may lower the velocity, in order to observe the effect of diffusivity. However, maintain this lower value of velocity in all of your cases so that the data points in the plots for this task have everything held constant except the parameter you are varying.

Task Three.

Select one of the process variables,

$$T_{in}\,,\ C_{A,in}\,,\ L\,,\ T_{surr}\,,\ D_R\,,\ v$$

Investigate how the reactor behavior changes as you change the variable. Discuss differences in both transient and steady-state behavior. Submit a plot which has on the x-axis the variable you are changing and on the y-axis the steady-state temperature and conversion. Vary the process variable over a range so that the effect of the variable is visible from the graphs.