

# A First Course on Kinetics and Reaction Engineering

## Unit 26. Analysis of Steady State PFRs

### Overview

Unit 26 describes how to write an accurate mathematical model for a reactor that obeys the assumptions of a plug flow reactor and that operates at steady state. It also provides a general approach for solving the resulting set of coupled ordinary differential equations. That approach is analogous to the approach for batch reactors and transient CSTRs. While the approach will likely need to be adapted to match the particular task at hand, it will allow an accurate quantitative analysis of steady state plug flow reactor processes.

### Learning Objectives

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Recognize problems wherein the reactor can be modeled as a steady state PFR
- Formulate the PFR design equations needed to model or design a specific reactor
- Identify the dependent and independent variables in the design equations for a steady state PFR
- Solve the steady state PFR design equations and use the results to perform requested reaction engineering or design tasks

### Information

The PFR design equations were derived in Unit 17, and it was noted that if the reactor operates at steady state, then all the derivatives with respect to time can be set equal to zero. The resulting steady state PFR design equations are reproduced here as equations (26.1) through (26.4). Equation (26.1) is a mole balance on species  $i$ , equation (26.2) is an energy balance on the entire PFR, and equations (26.3) and (26.4) are mechanical energy (momentum) balances on the reactor. Equation (26.3) is used if the reactor does not contain any packing, while equation (26.4) is used if the reactor constitutes a packed bed. Refer to Unit 17 if you are uncertain as to the meaning of any of the variables appearing in these equations.

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j \quad (26.1)$$

$$\pi DU(T_e - T) = \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i \hat{C}_{pi} \right) \frac{dT}{dz} + \frac{\pi D^2}{4} \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j) \quad (26.2)$$

$$\frac{dP}{dz} = -\frac{G}{g_c} \left( \frac{4}{\pi D^2} \right) \frac{d\dot{V}}{dz} - \frac{2fG^2}{\rho D} \quad (26.3)$$

$$\frac{dP}{dz} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right] \quad (26.4)$$

It can be seen above that the steady state PFR design equations form a set of coupled ordinary differential equations. If equation (26.3) is one of the design equations needed to model a particular plug flow reactor, then there will be one more dependent variable,  $\dot{n}_i$ ,  $T$ ,  $P$  and  $\dot{V}$ , than equations. A set of initial value ODEs cannot be solved unless the number of dependent variables is equal to the number of equations, hence either one variable must be re-expressed in terms of the others, or an additional equation must be added. Here we will use the former approach. If the fluid in the reactor is a liquid, it is very often acceptable to treat the liquid density as constant. In this case, the derivative of the volumetric flow rate with respect to axial position will equal zero. If the fluid is a gas, then the appropriate equation of state should be used. For example, if the fluid can be treated as an ideal gas, the derivative of the volumetric flow rate with respect to the axial position can be re-expressed using equation (26.5). Of course, the total molar flow rate is just the sum of the molar flow rates of each of the species, and the derivative of the total molar flow rate is just the sum of the derivatives of the molar flow rates of the species, equation (26.6).

$$\frac{d\dot{V}}{dz} = \frac{d}{dz} \left( \frac{\dot{n}_{total} RT}{P} \right) = \frac{RT}{P} \frac{d\dot{n}_{total}}{dz} + \frac{\dot{n}_{total} R}{P} \frac{dT}{dz} - \frac{\dot{n}_{total} RT}{P^2} \frac{dP}{dz} \quad (26.5)$$

$$\frac{d\dot{n}_{total}}{dz} = \sum_{\substack{i=all \\ species}} \frac{d\dot{n}_i}{dz} \quad (26.6)$$

Once the number of differential equations equals the number of dependent variables, the equations can be solved. Here we will assume that they can be written in the matrix form shown in equation (26.7) where the elements in the vector  $\underline{y}$  represent the dependent variables. In these equations,  $z$  is the independent variable, and it represents the axial distance from the inlet to the reactor. Typically, the values of the dependent variables,  $\underline{y}$ , will be known at  $z = 0$ . Thus, the design equations represent a set of initial value ordinary differential equations (ODEs). Except for a few very simple situations, it will not be possible to solve these equations analytically, so here it is assumed that all solutions will be obtained numerically.

$$\frac{d\underline{y}}{dz} = \underline{f}(\underline{y}, z); \quad \underline{y}(z=0) = \underline{y}^0 \quad (26.7)$$

There are many software packages that can be used to solve the design equations numerically, and you should use the one you feel most comfortable with. Supplemental Unit S5 presents a brief introduction to the numerical solution of initial value ODEs; if you aren't familiar with numerical solution of initial value ODEs, you should read Supplemental Unit S5. If you plan to use MATLAB to solve the design equations, Supplemental Unit S5 also presents template files that can be used to solve sets of initial

value ODEs of the form given in equation (26.7). No matter what software package you use, when the equations are written in the form of equation (26.7), you will need to provide three things as input to the software:

- the initial values of the dependent variables, that is, the values of each  $y_i$  at  $z = 0$
- the final value of either  $z$  or one of the dependent variables
- code that evaluates each of the functions,  $f_i$ , given a value for  $z$  and values for each of the dependent variables,  $y_i$

In some cases it may be known or stated that the pressure drop through the reactor is negligible, and in that situation, neither of the mechanical energy balance equations is needed. If the reactor operates isothermally, which is not all that common for commercial scale reactors, then the mole balance design equations can be solved separately from the energy balance equation (and for some problems the energy balance design equation won't be needed). Also, the design equations have been written above using the axial position,  $z$ , as the independent variable. In some situations it is preferable to use the reactor volume (which is equal to the fluid volume in a PFR) as the independent variable. This is easily accomplished. The volume and the axial position are related according to equation (26.8). As long as the reactor diameter is constant, differentiating equation (26.8) leads to equation (26.9) which can then be substituted into any of the design equations above. For example, substitution of equation (26.9) into the mole balance design equation (26.1) gives the equivalent mole balance design equation (26.10).

$$V = \frac{\pi D^2 z}{4} \quad (26.8)$$

$$dV = \frac{\pi D^2}{4} dz \quad (26.9)$$

$$\frac{d\dot{n}_i}{dV} = \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j \quad (26.10)$$

Because the design equations are initial value ODEs, solving the steady state PFR design equations is quite similar to solving the batch or transient CSTR design equations. It's always a good idea to start by converting all the known quantities into a consistent set of units. Making a schematic diagram and putting all the known information on the diagram can also be helpful. A mole balance, equation (26.1) should then be written for every species present in the system. At the same time, an energy balance on the reactor and a momentum balance should be written. After the equations have been written, they should be examined for terms that are zero-valued or negligible, and those terms should be eliminated.

One or more rates will appear in the design equations, and the code that is written to evaluate the design equations will need to use the corresponding rate expressions. The rate expressions will typically contain either concentrations or partial pressures of reagents in the reactor. Recalling that the code will be given values for the dependent variables, if partial pressures appear in the rate expressions, equation

(26.11) can be used to calculate their values, providing that the fluid behaves as an ideal gas. Similarly, if concentrations appear in the rate expressions, equation (26.12) can first be used. If the fluid phase is a liquid, it can often be assumed to have a constant density in which case equation (26.13) can be used, and if the fluid phase is an ideal gas, equation (26.14) can be used.

$$P_i = \frac{\dot{n}_i}{\sum_{k = \text{all species}} \dot{n}_k} P \quad (26.11)$$

$$C_i = \frac{\dot{n}_i}{\dot{V}} \quad (26.12)$$

$$\dot{V} = \dot{V}^0 \quad (\text{constant density liquid}) \quad (26.13)$$

$$\dot{V} = \frac{RT \left( \sum_{k = \text{all species}} \dot{n}_k \right)}{P} \quad (\text{ideal gas}) \quad (26.14)$$

The numerical solution of the design equations requires the final value of either the independent variable or one of the dependent variables. Solving the equations numerically will then generate values for the remaining independent and dependent variables. This procedure is straightforward if the unknown quantities are the outlet values of the dependent variables, but there could be situations where another parameter is unknown. For example, one might know the length of the reactor and the desired conversion of a reactant and be asked to find an inlet temperature that will lead to the specified conversion. In such cases, the procedure given here will need to be modified. In this case, one approach would be to use trial and error where the inlet temperature is guessed, the design equations are integrated from the inlet to the specified length of the reactor, and the conversion is compared to the desired value. The process is then repeated until the desired value is obtained. Equivalently, the design equations could be solved for a number of different inlet temperatures and a plot constructed of conversion versus inlet temperature. The inlet temperature needed to meet the problem specification could then be read from the plot. In short, every problem is unique and the general approach described here will likely need to be modified or adjusted when solving any one particular problem.