A First Course on Kinetics and Reaction Engineering
Unit 27. Analysis of Transient Plug Flow Reactors

Overview

Just as a CSTR occasionally must operate in a transient mode, so must a PFR. However, the corresponding modeling can be more challenging in the case of a PFR than it was for a CSTR. The reason for this is related to the kinds of equations needed to model the various reactors. For a CSTR, the steady state equations were algebraic, and to model transient CSTRs, ordinary differential equations were needed. With PFRs the steady state equations are ordinary differential equations, and the modeling of PFR transients requires one to solve partial differential equations. In light of the additional mathematical complexity and the introductory nature of this course, Unit 27 provides a thorough examination of setting up the equations needed to model a transient PFR, but it simply gives an overview of the solution of those equations. The unit also shows that certain kinds of PFR transients can be modeled precisely using only the steady state PFR design equations.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:
- discretization
- discretization point
- finite differences
- front
- break through

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:
- Identify and solve transient PFR problems that can and cannot be solved using only the steady state design equations
- Formulate the partial differential equations, initial conditions and boundary conditions needed to model a transient PFR
- Describe how the transient PFR design equations can be solved numerically

Information

The plug flow reactor design equations were derived in unit 17. They take the form of a set of coupled partial differential equations. Equation (27.1) is a plug flow reactor mole balance on species i, and equation (27.2) is the plug flow reactor energy balance design equation. As was the case for the steady state PFR energy balance, equation (27.2), as written, assumes that the sensible heat will be computed using the molar specific heat capacities of the individual species; in some cases the overall mass-specific or volume specific heat capacity of the fluid as a whole may be used instead.

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t} \tag{27.1}$$

$$\pi D U \left(T_e - T\right) = \left(\sum_{\substack{i=all \\ species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j\right)$$
$$+ \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all \\ species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2}{4} \frac{\partial P}{\partial t} \tag{27.2}$$

Transient plug flow reactor problems that require the use of equations (27.1) and (27.2) will not be solved in this course, but their solution will be described without going into the numerical details. You *will* learn how to formulate models for transient PFRs, though. There are some situations where a transient PFR can be analyzed using only the steady state design equations. This unit will describe how to identify this type of PFR transient, which you will be able to analyze.

Formulation of a model of a transient PFR is analogous to formulation of a steady state PFR model. One begins with the mole and energy balances above (along with a mechanical energy balance if pressure drop is significant). A mole balance is written for each species that appears in at least one chemical reaction as either a reactant or a product. Terms in the equations that are zero-valued or negligible are then eliminated, stoichiometric coefficients are substituted, and all the summations are expanded. An energy balance on the fluid in the reactor, i. e. equation (27.2) is then written and similarly simplified. If the specific heat capacity of the fluid as a whole is being used instead of the individual species' molar heat capacities, the two summations over all species are replaced with the product of the appropriate heat capacity and flow rate. Before solution can be attempted, one must additionally specify initial conditions (values, at the start of the transient, for each dependent variable as a function of the axial position) along with boundary conditions (values of each dependent variable at one of the ends of the reactor).

A common situation in reaction engineering involves determining the response of the reactor following some change in an operating parameter. In this situation, the initial state of the reactor system is known. That is, the molar flow rates and the temperature are known at all locations within the system. A parameter is then changed, and a transient plug flow reactor analysis is used to determine how the molar flow rates and the temperature change over time at all locations within the system. Most often, the design equations cannot be solved analytically, so a numerical approach is used. Here two such approaches will be outlined.

In both cases the solution begins by selecting a number of axial positions within the reactor. For example, the total length of the reactor might be divided into 100 equal increments of z. This is known as spatially *discretizing* the reactor. The value of each molar flow rate and the value of the temperature at each of these *discretization points* are treated as unknowns that vary over time. Thus, if the reactor was

divided into 100 points, there would be 100 unknown values of each molar flow rate and 100 unknown values of the temperature, and each of them would vary over time.

For the type of problem being considered here, the initial values of all these variables are known. That is, since we know the molar flow rate of each species and the temperature at all locations within the reactor just prior to the parameter being changed, we know the values of all these variables at time zero. The purpose of our analysis is to determine how each of these variables (at each location) evolve over time using the design equations. The design equations must be satisfied at every location within the reactor.

One approach is to approximate the derivatives of the molar flow rates and the temperature with respect to z using *finite differences*. That is, at each of the discretization points, the mole balance and energy balance design equations are written, but with the substitutions shown in equations (27.3) and (27.4). The deltas appearing in these equations can take various forms: forward differences, backward differences, central differences, etc. just as was done in differential analysis of kinetic data in Unit 14.

$$\frac{\partial \dot{n}_i}{\partial z} \cong \frac{\Delta \dot{n}_i}{\Delta z} \tag{27.3}$$

$$\frac{\partial T}{\partial z} = \frac{\Delta T}{\Delta z} \tag{27.4}$$

The result of making these substitutions is that all the derivatives with respect to z are replaced with algebraic expressions involving the molar flow rates and the temperatures at the discretization points. Consequently, only derivatives with respect to time remain, and so the equations have been transformed into ordinary differential equations. As already noted, the initial values of all the variables at all the discretization points are known, and so the system of ordinary differential equations can be solved in the same manner as the batch reactor design equations, the transient CSTR equations or the steady state PFR design equations. The only difference is that the number of simultaneous differential equations will be very much larger. Integrating this large system of equations will provide values for each of the unknowns at each of the discretization points as a function of time.

The method just described is called the method of lines. An alternative method for solving the equations is known as finite differences. The reactor is spatially discretized just as before. Then, only a very small interval of time is considered where the interval is so small that the derivatives with respect to time can be replaced by finite differences, equations (27.5) and (27.6). When this is done, the equations are no longer differential equations, they are algebraic. The algebraic equations are solved to get the values of all the unknown variables at the end of the short interval of time. These become the new initial values, and the process is repeated over and over, building up the time variation of each of the variables at each of the discretization points.

$$\frac{\partial \dot{n}_i}{\partial t} \cong \frac{\Delta \dot{n}_i}{\Delta t} \tag{27.5}$$

$$\frac{\partial T}{\partial t} = \frac{\Delta T}{\Delta t} \qquad\qquad\qquad (27.6)$$

Note that before applying either of these methods, the derivative of the volumetric flow rate with respect to time (in the mole balance) and the derivative of the pressure with respect to time (in the energy balance) would be re-written, for example using the ideal gas law if applicable. If there was significant pressure drop in the reactor, a transient form of the momentum balance would need to be added to the design equations. One should be aware that there are several variations on the two mathematical methods described here, as well as several other methods that can be used to solve the transient PFR design equations.

Having now described how the equations can be solved, it can be noted that in many cases it isn't necessary to do so. Remember, according to the assumptions made in defining a plug flow reactor, the fluid in a differentially thick cross section of the reactor does not mix in any way with the fluid in front of it, or with the fluid behind it. As such, when a fluid element like this enters the reactor, it doesn't "know" whether the million before it were just the same as it is (as would be the case at steady state), or whether it is the first fluid element of its kind (as would be the case if some step change had just occurred in one of the reactor's operating parameters (as would be the case at the beginning of a transient).

Suppose a PFR was initially filled with solvent, and then at time zero a solution containing reactant A started to flow into the reactor. Suppose further that A reacts adiabatically to produce B. Figure 27.1 plots the molar flow rate of A in the reactor as a function of axial position within the reactor at four different times. (The data used in this plot come from Example 1 of this unit.) Of course, at time zero, the molar flow rate of A is zero throughout the reactor because it is initially filled with solvent only. The green line shows the flow rate of A as a function of axial position after a period of time equal to one-fourth of the space time. You can see that A is present in the first one-fourth of the reactor at this time. The orange, blue and red lines show the flow rate of A as a function of axial position after periods of time equal to one-half of the space time, three-fourths of the space time and exactly the space time. The figure shows that a "front" moves through the reactor. Ahead of the front, only solvent is present as was the case prior to the start of the transient, while behind the front, the flow rate versus axial position is exactly equal to the final steady state profile. When the time just equals the space time, the front "*breaks through*" and emerges from the reactor, at which point the reactor has attained its final steady state.

In fact, if the initially present solvent had been at one temperature and the feed solution was at a different temperature, the PFR model would predict that a similar temperature front would progress through the reactor. Notice also, that the PFR model predicts that the duration of a transient will always be just equal to the space time of the reactor. In many cases, these predicted transients are not very realistic, and consequently more rigorous mathematical models are often used to simulate the transient behavior of a PFR. In particular, it is common to allow for some amount of axial mixing when analyzing transients in tubular reactors; if axial mixing is introduced into the design equations, the transient can then last longer than the space time.

As noted, the transient PFR design equations will not be solved in this course, mainly due to the additional time and effort required to solve them, but additionally because most transients can be

predicted from the steady state behavior before and after an operating parameter is changed. Based upon the discussion above, any change in concentration or temperature at the inlet to the reactor will lead to a front that moves through the reactor in a manner similar to that shown in Figure 27.1. The exception is a change in an operating parameter that affects the whole reactor, such as a change in the external temperature in a non-adiabatic PFR or a change in the inlet volumetric flow rate. Both of these changes would be "felt" by all of the elements in the reactor and would cause their evolution over time to differ from what it would have been in the absence of the change. For cases such as these the transient will not take the form of an abrupt front, and the transient PFR design equations need to be solved in order to analyze the transient. However, the duration of the transient would still equal the space time of the reactor if the plug flow model is used.
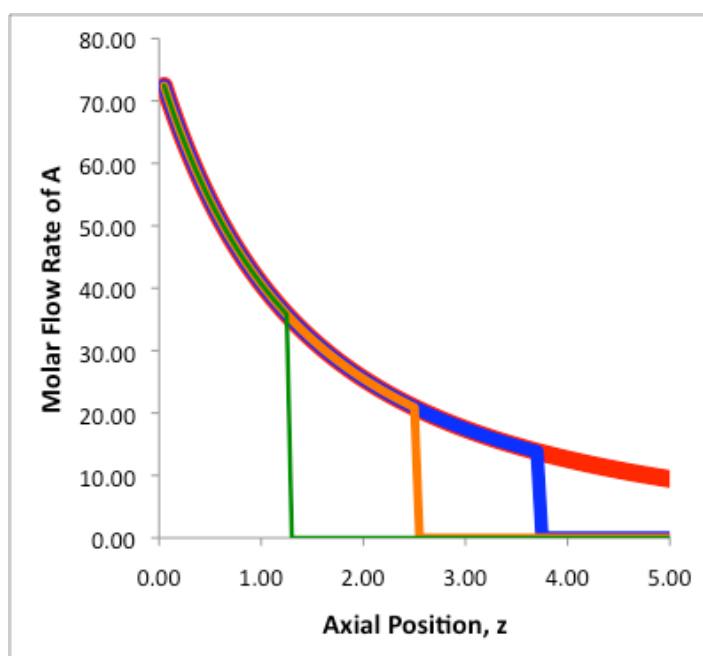

Figure 27.1. Molar flow rate of reactant A as a function of axial position at various times after the reactant began flowing into a solvent-filled reactor. The green line shows the profile after a time equal to one-fourth of the reactor space time has elapsed; orange corresponds to a time equal to one-half of the space time; blue, three-fourths of the space time, and red, a time equal to the space time.