A First Course on Kinetics and Reaction Engineering

Example 27.2

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. This example illustrates the formulation of the transient PFR design equations in a situation where the reactor cannot be analyzed using the steady state design equations.

Problem Statement

Recall the reactor from Example 1 of this unit. It is a perfectly insulated tubular reactor with a diameter of 10 cm and a length of 5 m being fed an aqueous solution containing A and B at concentrations of 1.0 and 1.2 M, respectively. This feed stream is at a constant temperature of 30 °C and flows at 75 L min^{-1}. Reagents A and B react according to reaction (1) with a rate of reaction that is accurately described by equation (2). The heat of reaction (1) is -10,700 cal mol^{-1} and may be assumed to be constant. The heat capacity of the solution and the density of the solution may be taken to be constant and equal to those of water (1.0 cal g^{-1} K^{-1} and 1.0 g cm^{-3}). The pressure drop in the reactor is negligible. Suppose that this reactor has reached steady state when suddenly the inlet volumetric flow rate is doubled to 150 L min^{-1}. Plot the molar flow rate of A and the temperature as a function of distance into the reactor 0.065 minutes after the feed was started, 0.131 minutes after the feed was started, 0.196 minutes after the feed was started and 0.262 minutes after the feed was started. (Note: the four times specified correspond to one-fourth of the space time, one-half of the space time, three fourths of the space time and the space time.)

$$\text{A} + \text{B} \rightarrow \text{Y} + \text{Z} \tag{1}$$

$$r_1 = \left(8.72\times10^5\ \text{L mol}^{-1}\ \text{min}^{-1}\right)\exp\left\{\frac{-7200\ \text{cal mol}^{-1}}{RT}\right\}C_AC_B \tag{2}$$

Problem Analysis

The problem describes a change in the feed to a PFR which will result in transient operation. This is not a kinetics problem because the rate expression is known; it is a transient PFR reaction engineering problem. To solve the problem it will be necessary to construct an accurate mathematical model for the reactor. However, in contrast to the first example of this unit, the change that is made here *does* affect all of the fluid elements in the reactor, not just the ones entering after the change. Specifically, when the flow rate is increased, all of the fluid within the reactor begins to flow faster. As a consequence, the transient will not take the form of a front that propagates through the reactor. That means that this problem cannot be solved simply by solving the steady state design equations. Instead, the transient forms of the mole and energy balance equations will be needed.

Problem Solution

The transient mole and energy balances were set up in Example 1 of this unit, so they are simply presented here as equations (3) through (7).

$$\frac{\partial \dot{n}_A}{\partial z} = -\frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_A}{\partial t} \tag{3}$$

$$\frac{\partial \dot{n}_B}{\partial z} = -\frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_B}{\partial t} \tag{4}$$

$$\frac{\partial \dot{n}_Y}{\partial z} = \frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_Y}{\partial t} \tag{5}$$

$$\frac{\partial \dot{n}_Z}{\partial z} = \frac{\pi D^2}{4} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_Z}{\partial t} \tag{6}$$

$$\frac{\partial T}{\partial z} = -\frac{\pi D^2 \Delta H_1}{4\rho_{fluid}\tilde{C}_{p,fluid}\dot{V}} r_1 - \frac{\pi D^2}{4\dot{V}} \frac{\partial T}{\partial t} \tag{7}$$

In order to solve these, it is necessary to specify the initial and boundary conditions. This is where the present example differs from Example 1. In this problem, the reactor is initially operating at steady state. Therefore, the steady state design equations must first be solved to determine the molar flow rate of each species and the temperature as a function of z. This steady state is the same as the one analyzed in Example 3 of Unit 26, so the analysis will not be duplicated here. In the remainder of this solution, the subscript "old.ss" will be used to denote a steady state value when the reactor was operating at the steady state prior to the change in inlet flow rate.

The initial conditions we need to specify are the molar flow rates and the temperature, each as a function of z, at the time when the change in flow rate has just been made. The temperature is easy; at the instant just after the inlet volumetric flow rate is doubled, the temperature at each location in the reactor will equal the temperature corresponding to the old steady state. This leads to the initial condition given in equation (8). The initial conditions for the molar flow rates are a little trickier, because when the volumetric flow rate is doubled, that changes all the molar flow rates, as well. There are two ways to understand what the molar flow rates (at any axial position, z) will equal at the instant just after the inlet volumetric flow rate is doubled. One is to realize that doubling the volumetric flow rate will double each molar flow rate as well. Hence, the initial values of the molar flow rates will equal two times the old steady state values. Another way to understand this is to note that the instant the volumetric flow rate is changed, the concentration at any one point will not change, and therefore the new molar flow rate will equal the old steady state concentration times the new volumetric flow rate, denoted by a subscript "new". The old steady state concentration is simply equal to the old steady state molar flow rate divided by the old steady state volumetric flow rate, leading to the initial conditions given in equations (9) through (12). Noting that the ratio of the new to old volumetric flow rates is two, we see that indeed, the molar flow rates are equal to two times the old steady state values.

$$\text{at } t = 0,\ T(z) = T_{old.ss}(z) \text{ for all } z \tag{8}$$

$$\text{at } t = 0,\ \dot{n}_A\left(z\right) = \left(\frac{\dot{n}_{A,old.ss}\left(z\right)}{\dot{V}_{old.ss}}\right)\dot{V}_{new} \text{ for all } z \tag{9}$$

$$\text{at } t = 0,\ \dot{n}_B\left(z\right) = \left(\frac{\dot{n}_{B,old.ss}\left(z\right)}{\dot{V}_{old.ss}}\right)\dot{V}_{new} \text{ for all } z \tag{10}$$

$$\text{at } t = 0,\ \dot{n}_Y\left(z\right) = \left(\frac{\dot{n}_{Y,old.ss}\left(z\right)}{\dot{V}_{old.ss}}\right)\dot{V}_{new} \text{ for all } z \tag{11}$$

$$\text{at } t = 0,\ \dot{n}_Z\left(z\right) = \left(\frac{\dot{n}_{Z,old.ss}\left(z\right)}{\dot{V}_{old.ss}}\right)\dot{V}_{new} \text{ for all } z \tag{12}$$

We also need to specify a boundary condition for each dependent variable that applies for all times after the change. In this problem, we have information about the dependent variables at the reactor inlet after the change, so we will specify the boundary conditions at z = 0. In fact, the only things that change from the old steady state inlet conditions are the inlet molar flow rates of A and B (their concentration stays the same while the volumetric flow rate doubles to $\dot{V}_{new}$). Since there isn't any Y or Z in the feed, their inlet flows remain equal to zero. The inlet temperature is also the same before and after the change. This leads to the boundary conditions given in equations (13) through (17).

$$\text{at } z = 0,\ \dot{n}_A = C_A^0\dot{V}_{new} \text{ for all } t > 0 \tag{13}$$

$$\text{at } z = 0,\ \dot{n}_B = C_B^0\dot{V}_{new} \text{ for all } t > 0 \tag{14}$$

$$\text{at } z = 0,\ \dot{n}_Y = 0 \text{ for all } t > 0 \tag{15}$$

$$\text{at } z = 0,\ \dot{n}_Z = 0 \text{ for all } t > 0 \tag{16}$$

$$\text{at } z = 0,\ T = 303.15 \text{ K for all } t > 0 \tag{17}$$

At this point the problem is set up for solution. In this course we will not ask students to solve equations of this type and we will not go into the details of solving them. Doing so would require discretization and application of finite differences or some equivalent approach. However, for illustrative purposes, the equations were solved numerically and will be presented here in order to show that while the transient still only lasts for one space time, it no longer takes the form of a front that propagates through the reactor. Figure 1 shows the profile of the molar flow rate of A along the reactor after 0.25, 0.5, 0.75 and 1.0 space times have elapsed. You can see that after one space time, the reactor is at the new steady state. The figure also shows the original steady state as a black curve.

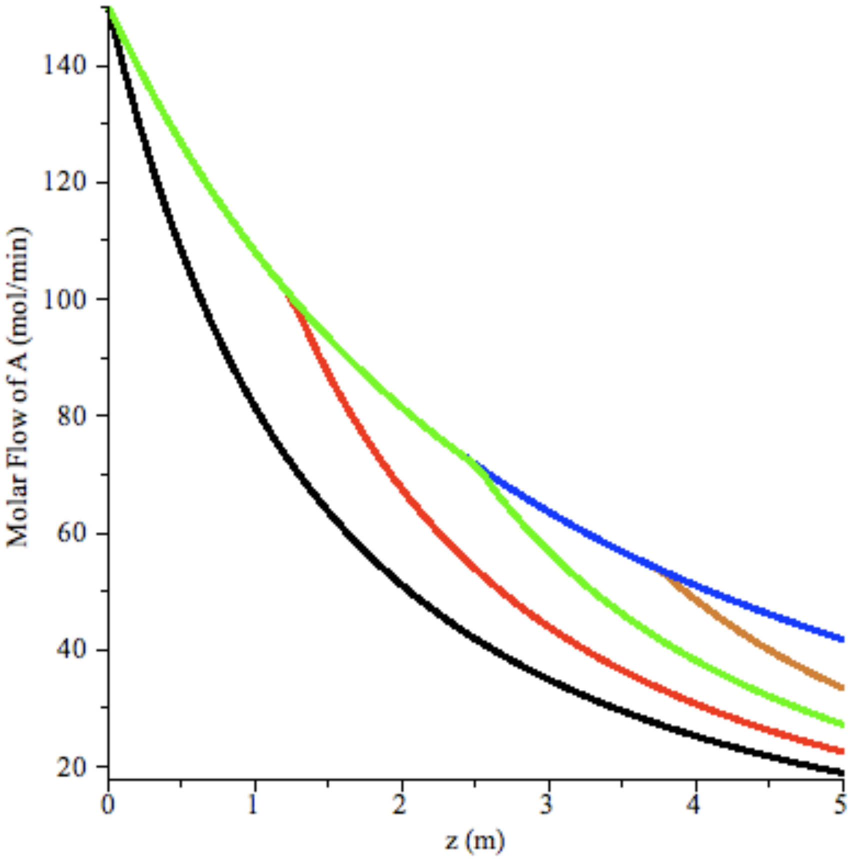

Figure 1. Profiles of the molar flow rate of A computed one-fourth of a space time after the change (red), one-half of a space time after the change (green), three-fourths of a space time after the change (brown) and one space time after the change (blue); the original steady state profile is shown in black.

Calculation Details

The numerical solution of the transient design equations goes beyond the scope of this course and will not be presented here.