A First Course on Kinetics and Reaction Engineering
Example 23.1

Problem Purpose

This problem illustrates the transient analysis of a CSTR following a change in an operating parameter.

Problem Statement

Recall the isothermal 4430 cm^3 steady-state chemostat that was analyzed in Example 22.3. It was fed a mixture of substrate and cells containing 0.04 g cm^{-3} of substrate and 8.0 x 10^{-5} g cm^{-3} of cell mass, and reached a steady state outlet cell mass concentration of 0.008 g cm^{-3} when the volumetric flow rate was 60 cm^3 min^{-1}. (Note: at these conditions, the steady state outlet mass flow of substrate is 1.35 g min^{-1}.) The rate of cell growth is given by equation (1) and the effective stoichiometry is that 2.2 grams of substrate are consumed per gram of call mass produced. Determine what would happen if the cells were suddenly removed from the feed and comment upon what you find. Then repeat the analysis for the case where the inlet volumetric flow rate is 59 cm^3 min^{-1}.

$$r = \frac{\left(0.014 \text{ min}^{-1}\right)[S][X]}{\left(0.001 \text{ g cm}^{-3}\right)+[S]} \tag{1}$$

Problem Analysis

This problem involves a CSTR, and the reaction kinetics are known, so it is a reaction engineering problem. The problem begins with the CSTR operating at steady state and asks what would happen if an operating parameter (the inlet cell mass concentration) was changed, therefore it is a transient CSTR problem. The reactor operates isothermally, so the mass balances can be solved independently of the energy balance, and in this case, there isn't sufficient information to write an energy balance. Therefore only the mass balance design equations will be solved to answer the question posed.

Problem Solution

Figure 1 shows a schematic representation of the reactor at the instant after the feed change has been made. The quantities provided in the problem statement are given in a consistent set of units, and they have been entered in the diagram. Notice that the inlet flows are all constant, and the reactor is already full at the time the transient begins. Since the reactor is already full at the start of the transient, the reaction volume is expected to be constant during the transient, and it is labeled accordingly in the schematic. Here it will be assumed that the fluid density is constant. With that assumption, the outlet volumetric flow rate will equal the inlet volumetric flow rate, and it, too, will be constant, as indicated in the schematic diagram.

At the steady state prior to the removal of the cell mass from the feed, Example 22.3 showed that the steady state outlet substrate mass flow rate was equal to 1.35 g min^{-1}. The steady state outlet cell

mass concentration was 0.008 g cm^{-3} and the volumetric flow rate is 60 cm^3 min^{-1}; multiplying these two quantities shows that the steady state outlet cell mass flow rate was 0.48 g min^{-1}. At the instant when the inlet cell mass concentration is set to zero and the transient response begins, there won't have been any time for these outlet mass flows to have changed, so these are the initial values of the transient outlet mass flows, as indicated in the schematic.
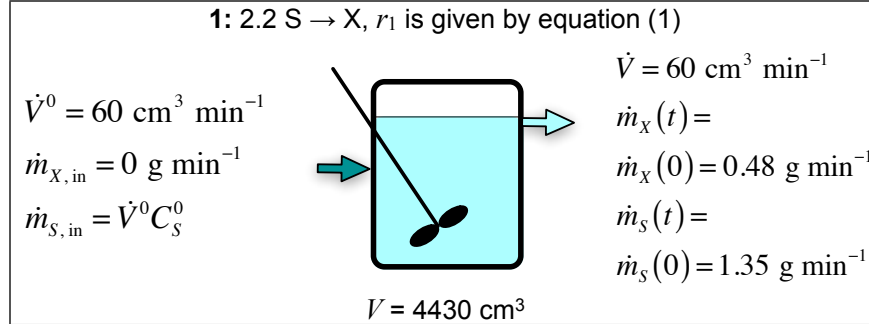
1: 2.2 S → X, r_1 is given by equation (1)

$$\dot{V}^0 = 60 \text{ cm}^3 \text{ min}^{-1}$$
$$\dot{m}_{X,\,in} = 0 \text{ g min}^{-1}$$
$$\dot{m}_{S,\,in} = \dot{V}^0 C_S^0$$

$$\dot{V} = 60 \text{ cm}^3 \text{ min}^{-1}$$
$$\dot{m}_X(t) =$$
$$\dot{m}_X(0) = 0.48 \text{ g min}^{-1}$$
$$\dot{m}_S(t) =$$
$$\dot{m}_S(0) = 1.35 \text{ g min}^{-1}$$

V = 4430 cm^3

Figure 1. Schematic representation of the CSTR.

Mass balances can be written for each species present in the system; given the effective stoichiometry of the reaction, these equations are effectively the same as the mole balances derived in Unit 17 with mass flow rates replacing molar flow rates. The generalized mass balance is given by equation (2). In this case, there is only one reaction taking place, so the summation reduces to a single term with j = 1. As already noted, the reaction volume and the volumetric flow rate are each constant, so their derivatives with respect to time are equal to zero. As a result, the generalized mass balance simplifies to equation (3).

$$\frac{V}{\dot{V}} \frac{d\dot{m}_i}{dt} + \frac{\dot{m}_i}{\dot{V}} \frac{dV}{dt} - \frac{\dot{m}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{m}_i^0 - \dot{m}_i + V \sum_{\substack{j= \text{ all} \\ \text{reactions}}} v_{i,j} r_j \tag{2}$$

$$\frac{V}{\dot{V}} \frac{d\dot{m}_i}{dt} = \dot{m}_i^0 - \dot{m}_i + V v_{i,1} r_1 \tag{3}$$

Writing this balance for X and for S in the standard form with only the derivative on the left of the equals sign leads to equations (4) and (5). In order to avoid confusing the inlet mass flows with the initial values of the outlet mass flows, the former have been denoted as $\dot{m}_{X,in}$ and $\dot{m}_{S,in}$ in equations (4) and (5). Equations (4) and (5) apply _after_ the change in the inlet cell mass concentration, so $\dot{m}_{X,in}$ is equal to zero.

$$\frac{d\dot{m}_X}{dt} = \frac{\dot{V}}{V} \left(\dot{m}_{X,in} - \dot{m}_X + V r_1 \right) \tag{4}$$

$$\frac{d\dot{m}_S}{dt} = \frac{\dot{V}}{V} \left(\dot{m}_{S,in} - \dot{m}_S - 2.2 V r_1 \right) \tag{5}$$

As noted in the problem analysis, the mass balances above will be solved independently of the energy balance. They are a set ordinary differential equations (ODEs). The independent variable is t, and the dependent variables are $\dot{m}_X$ and $\dot{m}_S$. The problem specification provides enough information to calculate the initial values of these dependent variables, so the design equations can be solved numerically using software for the solution of initial-value ODEs. Supplemental Unit S5 provides a brief overview of how such software works. There are many software packages you can use in order to do this; you should pick the one you are most comfortable using. No matter what software you elect to use, you will need to provide three things as input to that software:

- the initial values of the independent and dependent variables
- the final value of either t or one of the dependent variables
- code that evaluates each of the derivatives given a value for t and values for each of the dependent variables along with the additional information provided in the problem specification, that is, when the equations are written with the derivatives on the left hand side, as in equations (4) and (5), code that evaluates the right hand side of the equations given $\dot{m}_X$ and $\dot{m}_S$

First let's consider the initial values. These are the values of the dependent variables, $\dot{m}_X$ and $\dot{m}_S$, at the instant the inlet cell mass concentration is changed. At the instant the inlet cell mass concentration is changed, the outlet mass flows of X and S will still equal the steady state values from before the change, because there won't have been any time for them to change, yet. At the steady state before the change, the outlet cell mass concentration was 0.008 g cm^{-3}. Multiplying this outlet concentration by the volumetric flow rate gives the steady state outlet cell mass flow at the instant the inlet cell mass concentration was changed, equation (6). The problem states that the steady state outlet substrate mass flow was 1.35 g min^{-1}, equation (7).

$$\dot{m}_X\left(t=0\right)=C_{X,\text{ ss before}}\dot{V}=100C_X^0\dot{V} \tag{6}$$

$$\dot{m}_S\left(t=0\right)=1.35 \text{ g min}^{-1} \tag{7}$$

The second thing that must be provided in order to solve the design equations is either the final value of t or the final value of one of the dependent variables. In this problem, we are asked to describe the response of the system. To do so, a plot of the outlet cell mass flow rate versus time will be used. To make such a plot, a value of the elapsed time will be selected, and the equations will be solved to determine $\dot{m}_X$. Then a different value of the elapsed time will be selected, and the equations again will be solved to determine the corresponding value of $\dot{m}_X$. This will be repeated over a range of values of the elapsed time until the response stops changing, and the results will be plotted.

The final thing that must be provided in order to solve the design equations numerically is code that evaluates each of the derivatives given values for the independent and dependent variables and the other information provided in the problem statement. Looking at the mass balances, equations (4) and (5), the only quantities other than the dependent variables ($\dot{m}_X$ and $\dot{m}_S$) that appear on the right hand sides of

those equations are the volumetric flow rate ($\dot{V}$), the reaction volume (V), the inlet mass flow rates ($\dot{m}_{X,in}$ and $\dot{m}_{S,in}$) and the reaction rate (r_1). All of these quantities, except the reaction rate, are known constants. The reaction rate can be computed using equation (1), which introduces two additional quantities: the outlet mass concentrations of X and S (C_X and C_S). By definition, these can be calculated using equations (8) and (9).

$$[X] = C_X = \frac{\dot{m}_X}{\dot{V}} \tag{8}$$

$$[S] = C_S = \frac{\dot{m}_S}{\dot{V}} \tag{9}$$

At this point, all the input that is needed to solve the design equations numerically is available. Doing so as described above and plotting the results yields Figure 2 when the volumetric flow rate is equal to 60 cm^3 min^{-1}.

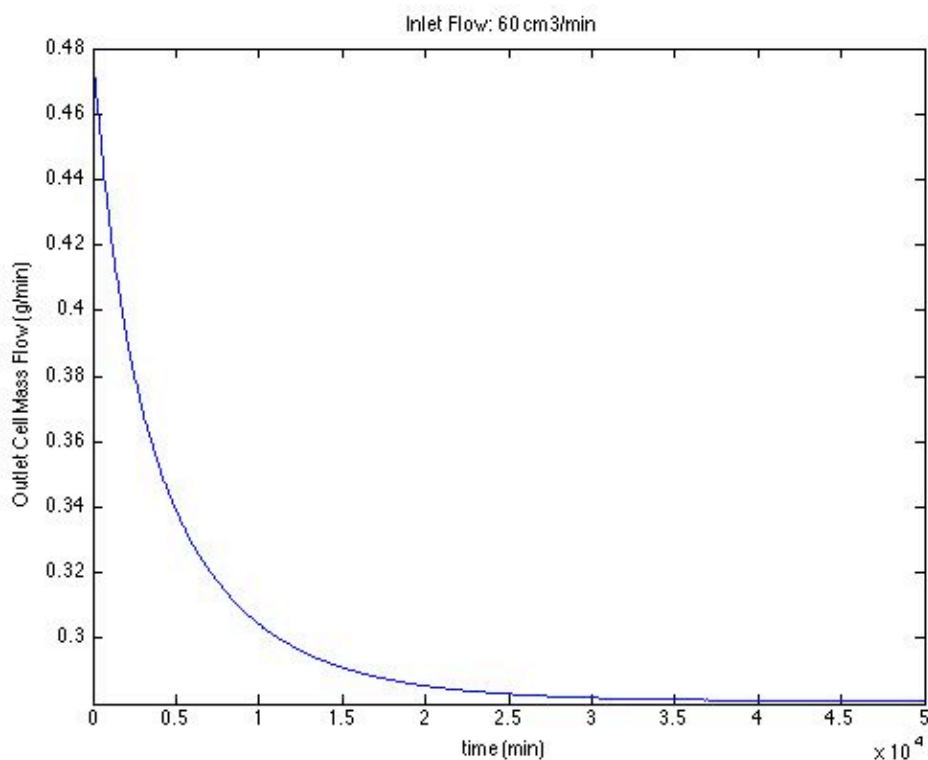*Figure 2. Response of the CSTR to removal of the cell mass from the 60 cm^3 min^{-1} feed.*

Figure 2 shows that the response extends over a very long time (~40000 min), and that eventually no cell mass remains in the outlet. This condition is known as wash out. It happens because the reaction is autocatalytic. At the steady state before the cell mass is removed from the feed, the rate of flow of cell

mass into the reactor together with the rate of cell mass generation within the reactor just equals the rate of flow of cell mass out of the reactor. When the cell mass is removed from the feed, this steady state is disrupted. More cell mass is flowing out of the reactor than is being produced in the reactor. This leads to a decrease in the concentration of cell mass within the reactor, and since the reaction is autocatalytic, this in turn decreases the rate of production of cell mass. That further reduces the amount of cell mass within the reactor, and as a consequence, the flow of cell mass from the reactor decreases. The critical question is whether the outflow of cell mass decreases faster or slower than the rate decreases. In this situation, the rate of reaction decreases faster than the outflow of cell mass, leading to smaller and smaller cell mass concentrations in the reactor, with eventual washout of all of the cell mass.

The problem also asks us what would happen if the volumetric flow rate was 59 cm^3 min^{-1} instead of 60 cm^3 min^{-1}. The first thing that must be recognized is that if the flow rate was 59 cm^3 min^{-1}, then the average residence time would be longer than with a flow rate of 60 cm^3 min^{-1}. As a consequence, the steady state outlet cell mass flow rate before the change in inlet concentration will be greater at a volumetric flow rate of 59 cm^3 min^{-1} than at a flow rate of 60 cm^3 min^{-1}. Similarly, the steady state outlet substrate flow rate will be smaller at a volumetric flow rate of 59 cm^3 min^{-1} than at a flow rate of 60 cm^3 min^{-1}. Therefore, the initial values of the outlet mass flow rates will be different from the values used above.

Example 22.3 was therefore re-solved, but with the reaction volume equal to 4430 cm^3 and with the outlet flow rate of cell mass unknown. The details will not be presented here, but the result was that the steady state outlet cell mass flow is 0.62 g min^{-1} and the outlet flow of substrate is 1.0 g min^{-1}. The analysis described above was then repeated using these values as the initial values and using a volumetric flow rate of 59 cm^3 min^{-1}. The results are shown in Figure 3, where it can be seen that washout no longer occurs. Instead, the outlet cell mass falls to a new, non-zero steady state level. The reason for this difference can be explained as before. Removing the cell mass from the feed again leads to an imbalance where the outflow of cells is greater than the rate of their production. In this case, however, the decrease in cell mass within the reactor causes the outflow of cell mass to decrease more rapidly than the rate so that eventually they reach a point where steady state is re-established.
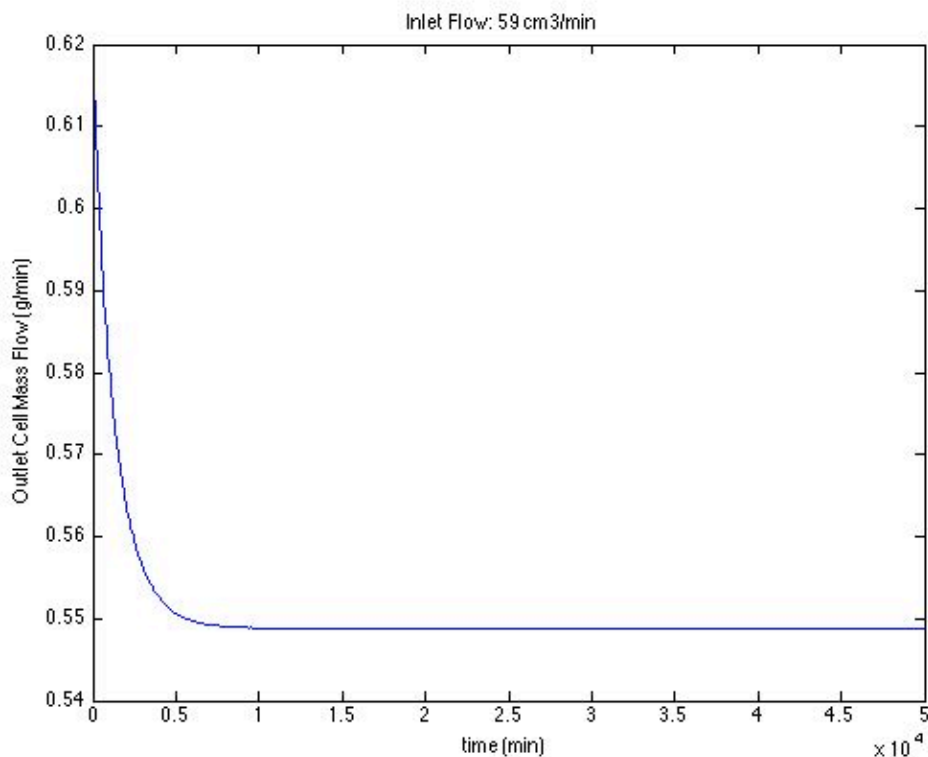
Figure 3. Response of the CSTR to removal of the cell mass from the 59 cm^3 min^{-1} feed.

Calculation Details Using MATLAB

If you elect to use MATLAB to solve the design equations, Supplemental Unit S5 provides template files that can be used. In this problem, the equations are initial value ODEs and the final value of the independent variable is provided, so the appropriate template file is SolvIVDifl.m. Before that file can be used, you must make four required modifications. Here I will also describe a few non-required modifications that you might want to consider when solving problems of this type.

To begin, I made a copy of the template file and saved it as Example_23_1.m; a copy of that file accompanies this solution. Since the function name must match the filename, I changed the name of the function to Example_23_1. At the same time, knowing that I won't need to use the results from these calculations in subsequent calculations, I changed the function so that it does not return any values. However, I knew I'd want to run it for two different volumetric flow rates with their corresponding initial outlet mass flow rates, so I modified the function to accept the volumetric flow rate and the two initial outlet mass flow rates as arguments. The template file begins with a long set of comments describing what it does and how to use it; I replaced these comments with a brief comment stating the purpose of the modified version. None of these modifications were required. The first _required_ modification involves entering all the known quantities from the problem statement along with constants that will be needed (from handbooks or other reference sources). As these are entered, they should be converted to a

consistent set of units. For this problem, I decided to use units of cm^3, min and g. The result of making all these modifications is shown in Listing 1.

```
% Modified version of the MATLAB template file SolvIVDifI.m used in the
% solution of Example 23.1 of "A First Course on Kinetics and Reaction
% Engineering."
%
function Example_23_1(VFR, mXout0, mSout0)
    % Known quantities and constants (in consistent units)
    CS0 = 0.04; % g/cm3
    mSin = VFR*CS0; % g/min
    mXin = 0; % g/min
    V = 4.430e3; % cm3
```

Listing 1. Initial comment, function declaration and known constants after modification of SolvIVDifI.m

The second _required_ modification involves entering the code to evaluate the right hand side of the ODEs when they are written in the form shown in equation (10). Notice that the equations are provided as a vector quantity. Thus, it is necessary to map the dependent variables used in the problem statement ($\dot{m}_X$ and $\dot{m}_S$) to a vector z, and the corresponding derivatives are mapped to a vector dzdt. I find it useful at the start of the internal function that will evaluate the derivatives, to define local variables with the names used in the problem statement. This modification is not required, but in my opinion, it makes the code more readable and easier to debug. In addition, the resulting list of variables serves as a reminder of the mapping of the problem statement variables to the vector z. The required code first calculates the two outlet mass concentrations that appear in the rate expression according to equations (8) and (9). Following that, the rate can be calculated using equation (1). Finally, the derivatives are evaluated using equations (4) and (5), saving the results in the vector dzdt. The resulting code is shown in Listing 3.

$$\frac{d\underline{z}}{dt} = \underline{f}(\underline{z}, t) \tag{10}$$

```
    % Function that evaluates the ODEs
    function dzdt = odeqns(t,z)
        mXout = z(1);
        mSout = z(2);
        CX = mXout/VFR;
        CS = mSout/VFR;
        r = 0.014*CS*CX/(0.001 + CS);
        dzdt = [
            VFR/V*(mXin - mXout + V*r)
            VFR/V*(mSin - mSout - 2.2*V*r)
        ];
    end % of internal function odeqns
```

Listing 3. Results of the second required modification.

The third _required_ modification involves providing the initial values of the independent and dependent variables and the final value of the independent variable. The initial values of the dependent

variables are entered as a vector named z0, and they must use the same mapping of the problem variables to the vector z0 as was used previously for z. The results of performing this modification are shown in Listing 4. A large value was selected for the final time so that the full evolution of the outlet cell mass flow could be plotted.

```
% Initial and final values
t0 = 0;
z0 = [
    mXout0
    mSout0
];
tf = 50000; % min
```

Listing 4. Results of the third required modification.

The fourth and final <u>*required*</u> modification is to use the results from solving the ODEs to calculate whatever the problem requested. In this case, code was added to plot the outlet cell mass flow versus elapsed time, as shown in Listing 5.

```
% Plot the outlet cell mass flow versus time
figure
plot(t,zz(:,1))
title(['Inlet Flow: ',num2str(VFR),' cm3/min'])
xlabel('time (min)')
ylabel('Outlet Cell Mass Flow (g/min)')
```

Listing 5. Results of the fifth required modification.

Once the file containing all the modifications had been saved, it was executed by typing Example_23_1(60, 0.48, 1.35) at the MATLAB command prompt. The three arguments are the values of the volumetric flow rate in cm^3 min^{-1}, the initial value of the outlet cell mass flow rate in g min^{-1} and the initial value of the outlet substrate mass flow rate in g min^{-1}. Doing so generated Figure 2 as output; it was executed a second time using 59, 0.62 and 1.0 as the argument, leading to Figure 3. The code used to calculate the steady state outlet mass flow rates for a volumetric flow rate of 59 cm3 min-1 will not be discussed here, but it accompanies this solution as Example_23_1_ss.m. It is a simple modification of the code used in Example 22.3 with the only differences being that the reactor volume was known while the outlet flow of cell mass was not.