

## A First Course on Kinetics and Reaction Engineering

### Example 11.4

#### Problem Purpose

This problem illustrates the use of the age function measured using an impulse stimulus to test whether a reactor conforms to the assumptions of the ideal CSTR model.

#### Problem Statement

Suppose you plan to use a 12 L laboratory reactor to generate kinetics data. Before doing that, you establish a steady flow of water at a rate of  $6 \text{ L min}^{-1}$ . A stopwatch is then started just as 24 g of a tracer is instantly added to the reactor inlet. The concentration of tracer in the outlet is then measured versus time. Show how to use the resulting data, below, to decide whether the reactor can be modeled as a CSTR.

Time (min)	Concentration (g/L)
0.2	0.04
0.4	1.97
0.6	1.76
0.8	1.47
1	1.36
1.2	1.26
1.4	1.08
1.6	0.91
1.8	0.88
2	0.70
2.2	0.56
2.4	0.64
2.6	0.50
2.8	0.48
3	0.45
5	0.14
7.5	0.03
10	0.05

### Problem Analysis

The experiment described in the problem statement involves the application of an impulse stimulus to the reactor. The data can therefore be used to calculate the age function for the reactor, and the result can be compared to the age function that would be expected if the reactor is an ideal CSTR.

### Problem Solution

When an impulse stimulus is used, the age function is found using equation (1). The times given in the table represent the time elapsed since the application of the stimulus ( $t_0 = 0$  min), and consequently they are equal to  $\lambda$ . The total mass used in the impulse is given as  $m_{tot} = 24$  g, and before and after the impulse, there was no tracer in the feed, so  $w_0 = 0$ . The fluid flowing in the reactor is water, and its volumetric flow rate is given, so its mass flow rate can be found through use of the density of water as shown in equation (2). The data table gives mass concentrations in the reactor outlet; these are related to the mass fraction in the outlet according to equation (3)

$$F(t' - t_0) = F(\lambda) = \frac{\dot{M} \int_{t_0}^{t'} (w_{out}(t) - w_0) dt}{m_{tot}} \quad (1)$$

$$\dot{M} = \dot{V} \rho = \left( 6 \frac{\text{L}}{\text{min}} \right) \left( 1000 \frac{\text{g}}{\text{L}} \right) = 6000 \frac{\text{g}}{\text{min}} \quad (2)$$

$$w_{out}(t) = \frac{C_{out}(t)}{\rho} = \frac{C_{out}(t)}{1000} \frac{\text{L}}{\text{g}} \quad (3)$$

After substitution of these known quantities and relationships, equation (1) simplifies to equation (4). Thus, for each entry in the table for a given  $\lambda = t$ , equation (4) can be used to calculate the corresponding value of the age function. Notice that the units of the integral will cancel out the units preceding the integral giving a dimensionless age function, as expected.

$$F(\lambda) = \frac{6000 \int_0^{\lambda} \left( \frac{C_{out}(t)}{1000} \frac{\text{L}}{\text{g}} - 0 \right) dt}{24} \text{ min}^{-1} = \left( 0.25 \frac{\text{L}}{\text{g min}} \right) \int_0^{\lambda} C_{out}(t) dt \quad (4)$$

Since we do not have a functional form for  $C_{out}$ , but instead, a set of discrete values, the integration must be performed numerically, for example by use of the trapezoid rule. Figure 1 illustrates the evaluation of the integral in equation (4) using the trapezoid rule. First, since the integrals begin at  $t = 0$ , a data point is added at the top of the table ( $t = 0$ ,  $C = 0$ ) since we know that there is no tracer in the outlet at the time the impulse is applied. To perform the integration,  $C$  is plotted versus  $t$ , as shown in the figure, and the data points are connected with straight line segments. The integral from  $t = 0$  to  $t = 0.2$  (the first

data point) is then taken to equal the area of the red trapezoid in Figure 1. The integral from  $t = 0$  to  $t = 0.4$  is taken to equal the area of the red trapezoid plus the area of the blue trapezoid. The integral from  $t = 0$  to  $t = 0.6$  is taken to equal the area of the red trapezoid plus the area of the blue trapezoid plus the area of the green trapezoid, and so on. The application of the trapezoid rule to evaluate equation (4) can be performed manually, using a spreadsheet or using mathematics software, and a value for  $F(\lambda)$  can be calculated for each data point in the data table.

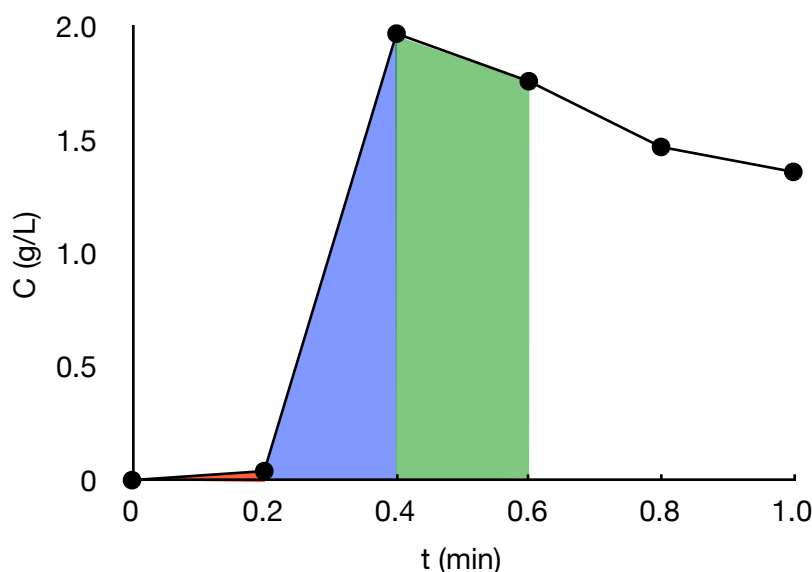


Figure 1. Integration using the trapezoid rule.

We wish to compare the experimental age function to that for a corresponding ideal CSTR. For an ideal CSTR, the age function is given by equation (5). The average residence time,  $\bar{t}$ , that appears in equation (5) is found using equation (6).

$$F_{CSTR}(\lambda) = 1 - \exp\left\{\frac{-\lambda}{\bar{t}}\right\} \quad (5)$$

$$\bar{t} = \frac{V}{\dot{V}} \quad (6)$$

The problem statement gives the values of the volume ( $V = 12$  L) and the volumetric flow rate ( $\dot{V} = 6$  L min<sup>-1</sup>), so equation (5) can be calculated for any value of  $\lambda$ .

In order to test whether the laboratory reactor obeys the assumptions of an ideal CSTR, the values of  $F(\lambda)$  calculated for the laboratory reactor using equation (4) can be plotted as a function of  $\lambda$ . On the same set of axes, the CSTR age function, calculated using equation (5), can also be plotted. The resulting plots are shown in Figure 2. The figure shows that the experimental data deviate significantly from the values expected for an ideal CSTR, so the reactor should not be modeled as an ideal CSTR.

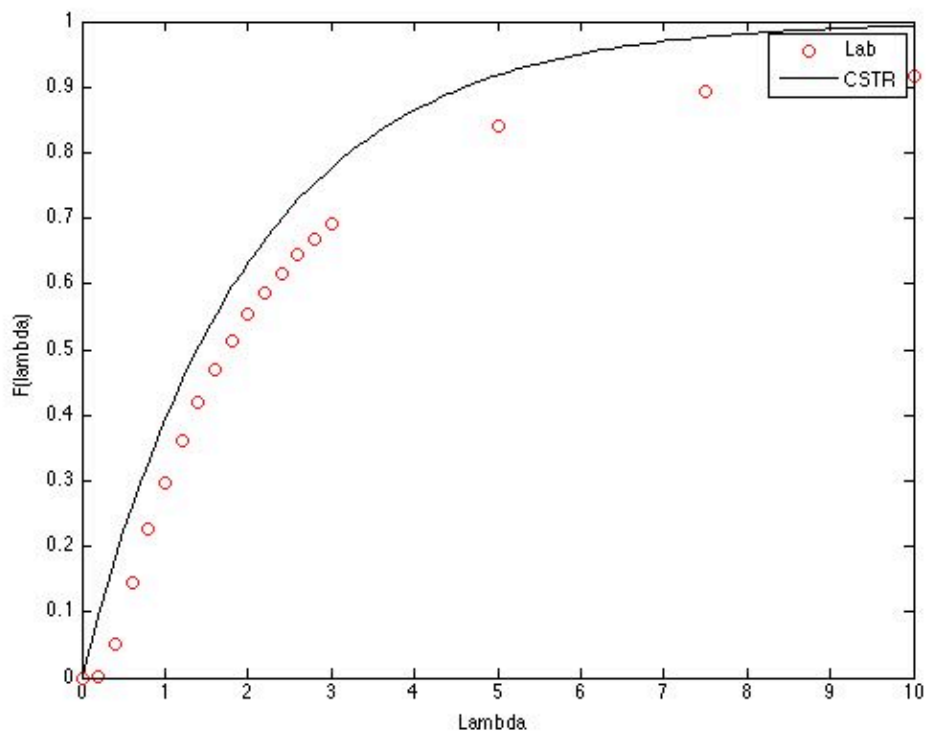


Figure 2. Comparison of the experimental and ideal age functions.

### Calculation Details Using MATLAB

The calculations required for the solution of this problem are easily accomplished using MATLAB. A MATLAB file named Example\_11\_4.m that performs the calculations accompanies this solution. The values of constants appearing in the problem are entered first. Noting that I would need to integrate starting from  $t = 0$ , I added a data point at the top of the table ( $t = 0$ ,  $C = 0$ ) as I entered the data from the first column of the data table as a vector named  $t$  and the data from the second column of the data table as a vector named  $C$ . This can be seen in Listing 1.

```

% Constants
V = 12; % L
VFR = 6; % L/min
m_tracer = 24; % g
rho = 1000; % g/L
MFR = VFR*rho; % equation (2)

% Experimental data from the table, adding in values for t = 0
t = [0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
5
7.5
10];

C = [0
0.04
1.97
1.76
1.47
1.36
1.26
1.08
0.91
0.88
0.70
0.56
0.64
0.50
0.48
0.45
0.14
0.03
0.05];

```

*Listing 1. Entry of the data from the problem statement.*

MATLAB has a built-in function named `trapz` that will perform numerical integration using the trapezoid rule. We know that the value of  $F(\lambda)$  is zero for the first data point ( $t = 0$ ,  $C = 0$ ). The only “trick” for using this function in the present case is to notice that when we calculate  $F(\lambda)$  for the second data point using equation (4), we want to integrate from  $t = 0$  to  $t = 0.2$ . These are the first two values of the MATLAB arrays `t` and `C`, entered earlier. Therefore, for this data point, we only want `trapz` to integrate over the first 2 elements in those arrays. When we calculate the third data point we want to include the

first 3 data points in the integral, so we want `trapz` to integrate over the first 3 elements in the arrays `t` and `C`, and so on. The code in Listing 2 accomplishes this integration for all of the data points.

```
% Calculate F using equation (4)
F = zeros(length(t),1);
F(1) = 0.;
for i = 2:length(t)
    F(i) = MFR/rho/m_tracer*trapz(t(1:i),C(1:i));
end
```

*Listing 2. Calculation of the age function for the laboratory reactor.*

We can calculate data points for the age function of the CSTR as a function of  $\lambda$  using equation (5). We want to plot these values as a line, not as data points. If we use too few data points, the plot will not be smooth, it will look like a set of connected straight line segments. Therefore, for this calculation we use more data points than are given in the data table, but the data points we use span the same range. MATLAB provides a built-in function named `linspace` that will create an array of 100 evenly spaced points between two specified endpoints, so in Listing 3, the age function for an ideal CSTR is calculated for 100 data points using equation (5).

```
% Calculate F_CSTR using equation (5), but with more data points so that a
% smooth curve results
t_CSTR = linspace(t(1),t(length(t)));
F_CSTR = zeros(length(t),1);
t_bar = V/VFR;
for i = 1:length(t_CSTR)
    F_CSTR(i) = 1-exp(-t_CSTR(i)/t_bar);
end
```

*Listing 3. Calculation of the age function for an ideal CSTR.*

At this point, the only task remaining is to plot the results. For that, standard MATLAB plot commands are used, and Figure 1 shows the result. The plotting commands are included in the file `Example_11_4.m` which accompanies this example.