# A First Course on Kinetics and Reaction Engineering

## Example 11.5

### Problem Purpose

This problem illustrates the use of the age function measured using a step change stimulus to test whether a reactor conforms to the assumptions of the ideal PFR model. Then it shows that for a PFR, it is actually much easier to work with the response directly.

### Problem Statement

A former employee of your company studied the kinetics of a reaction using a laboratory reactor that was modeled as an ideal PFR. A pilot plant was built using the resulting rate expression, but the pilot plant is not performing as expected, so an experiment was conducted for the purpose of determining whether the laboratory reactor obeys the assumption of an ideal PFR. This should have been done before the reaction kinetics were studied; that's probably why it's a ***former*** employee. A steady flow of 6 g min$^{-1}$ of a 2 M aqueous solution of a dye tracer was established in the 23 cm$^3$ reactor. Then the feed dye concentration was suddenly changed to 10 M and the outlet dye concentration was measured as a function of time. The data in Table 1 were recorded. Can the laboratory reactor can be accurately modeled as an ideal PFR?

| ***Time (min)*** | ***Conc (M)*** |
|---|---|
| 0.50 | 2.1 |
| 1.00 | 2.0 |
| 1.50 | 2.1 |
| 2.00 | 2.0 |
| 2.50 | 2.0 |
| 3.00 | 1.9 |
| 3.50 | 4.4 |
| 4.00 | 7.8 |
| 4.50 | 9.1 |
| 5.00 | 9.8 |
| 5.50 | 10.0 |
| 6.00 | 10.0 |
| 6.50 | 10.1 |
| 7.00 | 10.0 |
| 7.50 | 9.9 |
| 8.00 | 10.0 |
| 8.50 | 10.0 |
| 9.00 | 9.9 |
| 9.50 | 10.0 |
| 10.00 | 10.0 |

*Table 1. Experimentally measure outlet dye concentrations.*

### Problem Analysis

In the experiment described in the problem statement, the inlet dye concentration was instantaneously changed from one value to another. This is a step change stimulus, so the response can be used to compute the age function for the laboratory reactor. That can be compared to the age function that would be expected if the reactor obeys the ideal PFR assumptions to decide whether it is safe to model the reactor as an ideal PFR.

**Problem Solution**

The stimulus is a step change so the experimental age function is calculated using equation (1). In equation (1) $w$ represents the outlet weight fraction of dye with the subscripts $0$, $t$ and $f$ denoting the elapsed time at the point were the stimulus was applied, $t$ minutes after the stimulus was applied and after an infinite period of time, respectively. The times given in Table 1 equal the time elapsed since the application of the stimulus, hence $\lambda$ = $t$.

$$F\left(\lambda = t\right) = \frac{w_t - w_0}{w_f - w_0} \tag{1}$$

By definition, the outlet dye weight fraction is equal to the outlet dye mass flow rate, $\dot{m}$, divided by the outlet total mass flow rate, $\dot{M}$, as given in equation (2). The outlet dye mass flow rate is equal to the outlet dye molar flow rate, $\dot{n}$, times the molecular weight of the dye, $M_{dye}$, as written in equation (3). The outlet dye molar flow rate can be expressed in terms of the outlet volumetric flow rate, $\dot{V}$, and the outlet dye concentration, $C$, as in equation (4). Finally, the outlet volumetric flow rate is equal to the outlet total mass flow rate divided by the density of the fluid, equation (5). When all these equations are combined and substituted for the weight fractions appearing in equation (1), equation (6) results (assuming the fluid density to be constant).

$$w = \frac{\dot{m}}{\dot{M}} \tag{2}$$

$$\dot{m} = \dot{n} M_{dye} \tag{3}$$

$$\dot{n} = \dot{V} C \tag{4}$$

$$\dot{V} = \frac{\dot{M}}{\rho_{fluid}} \tag{5}$$

$$F\left(\lambda = t\right) = \frac{C_t - C_0}{C_f - C_0} \tag{6}$$

According to the problem statement, $C_0$ = 2 M and $C_f$ = 10 M, and values for $C_t$ are provided in Table 1, so a value of $F(\lambda)$ can be calculated for each $t$ (= $\lambda$) value in Table 1.

We want to compare those values to the age function predicted by the ideal PFR model, equation (7). The average residence time that appears in equation (7) can be calculated as shown in equation (8) if one assumes that the density of the fluid remains equal to that of water. Hence, for the ideal PFR, the age function equals zero for $\lambda$ < 3.38 min and it equals 1 for $\lambda$ greater than or equal to 3.83 min.

$$F_{PFR}\left(\lambda\right) = 0 \text{ for } \lambda < \bar{t}$$
$$F_{PFR}\left(\lambda\right) = 1 \text{ for } \lambda \geq \bar{t} \tag{7}$$

$$\bar{t} = \frac{V}{\dot{V}} = \frac{23\text{ cm}^3}{\left(6\text{ g min}^{-1}\right)\left(1\text{ g cm}^{-3}\right)} = 3.83\text{ min} \tag{8}$$

A plot of the two age functions is shown in Figure 1. From the plot it appears that there may be some mixing in the experimental reactor, and consequently it may not be well represented using an ideal PFR model.

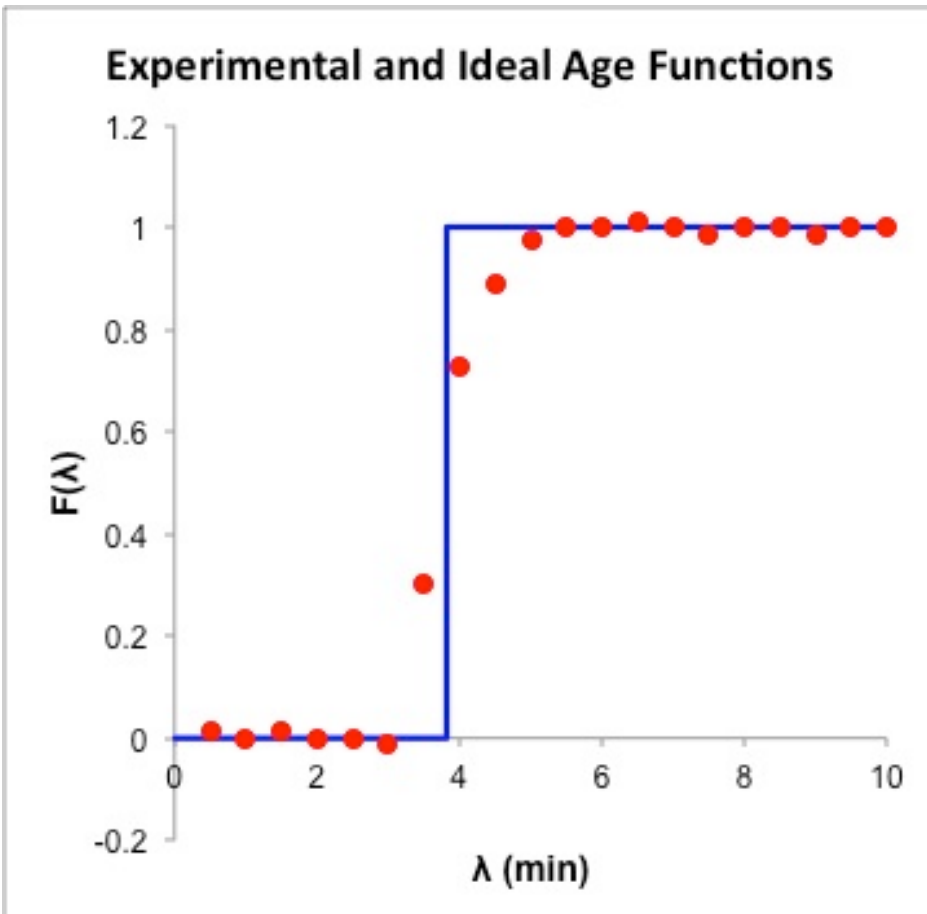


*Figure 1. Comparison of the age function for the laboratory reactor (red) to that for an ideal PFR (blue).*

If you think about it for a moment, there is a much easier way to assess whether a given reactor obeys the assumptions of an ideal PFR. In the absence of reaction, the steady state PFR model assumes that whatever enters the reactor will flow through the reactor and emerge unchanged, since there is no axial mixing. The time required for flowing through the reactor is just the average residence time as given in equation (8). Thus, for any stimulus, the ideal PFR model predicts that the outlet tracer concentration at time $t$ should exactly equal the inlet tracer concentration at time $t$ minus $\bar{t}$ , equation (9).

$$C_{in}\left(t-\bar{t}\right)=C_{out}\left(t\right) \tag{9}$$

Hence plots of $C_{in}\left(t-\bar{t}\right)$ and $C_{out}\left(t\right)$ versus t should superimpose if the reactor behaves as an ideal PFR. Figure 2 shows such a plot for this problem. At first glance, Figure 2 looks the same as Figure 1. In fact, the only difference between the two figures is the vertical scale. The age function is dimensionless and ranges from 0 to 1 while the $y$-axis in Figure 2 has units of concentration and, for this problem, ranges approximately from 2 M to 10 M.

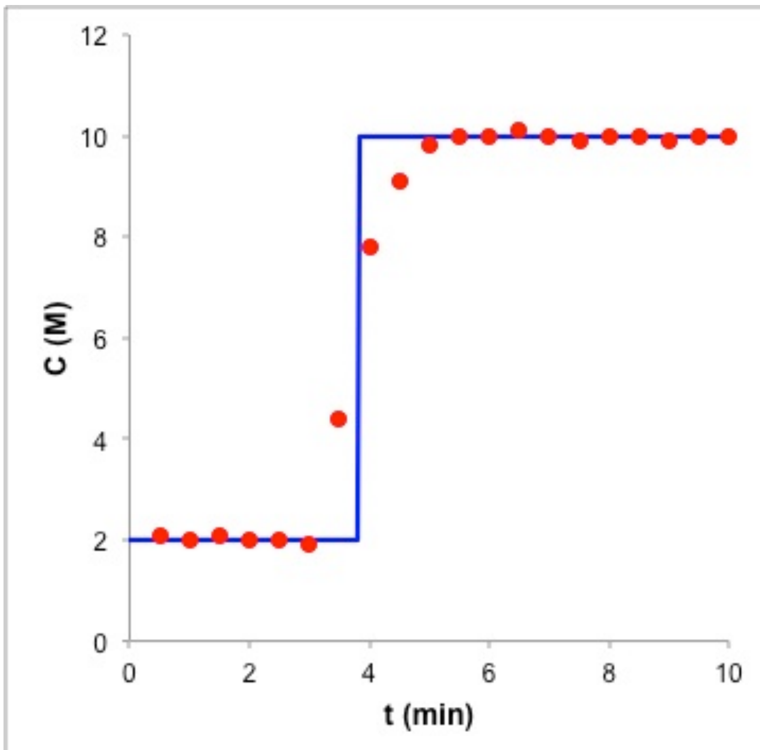


*Figure 2. Comparison of the outlet tracer concentration at time $t$ (red) to the inlet tracer concentration at time $t$ minus $\bar{t}$ (blue).*

Clearly, the information content of Figure 2 is the same as that for Figure 1, and Figure 2 was generated without doing any calculations. If the only reason for performing the stimulus-response experiment is to decide whether or not a given laboratory reactor can be safely modeled as a PFR, then it is acceptable and faster to use a plot like that in Figure 2. In this case the problem statement indicates that the experimental kinetics data have already been collected using the reactor that does not conform to the ideal PFR assumptions. In this situation, it might be preferable to use the age function as in Figure 1, because it may prove helpful in generating a different model (other than the ideal PFR model) for the laboratory reactor. If that proved possible, then the existing kinetics data could be analyzed using that different model. Part IV of this course examines reactor models other than the ideal batch reactor, CSTR and PFR, and in some cases these models make use of the age function for the reactor.