A First Course on Kinetics and Reaction Engineering

Example 36.1

Problem Purpose

This problem illustrates the use of the late-mixing segregated flow model to represent a non-ideal reactor. It also contrasts the late-mixing segregated flow model and the ideal CSTR model.

Problem Statement

The irreversible elementary reaction in equation (1) occurs isothermally in a non-ideal reactor. At the reactor temperature the reaction is second order in A, and the rate coefficient is equal to 0.5 L mol^{-1} min^{-1}. The reactor volume is 25 L, and the feed consists of 4 L min^{-1} of a solution containing A at a concentration of 2.3 mol L^{-1}. The age function for this reactor has been measured and is given in equation (2). Use a late-mixing segregated flow model to compute the conversion in the reactor.

$$\text{A} \rightarrow \text{Z} \tag{1}$$

$$F(\lambda) = 1 - \exp(-0.16\lambda) \tag{2}$$

Problem Analysis

The problem statement tells us to apply a segregated flow model to a reactor, so the type of problem is clear. To find the answer, we will first model the fluid elements as ideal isothermal batch reactors to find an expression for the conversion as a function of fluid element residence time. We will then use that expression in the late-mixing segregated flow model equation to compute the conversion for the reactor as the average over all of the individual fluid elements.

Problem Solution

Reading through the problem statement one finds that the following quantities are specified: k = 0.5 L mol^{-1} min^{-1}, V = 25 L, $\dot{V}$ = 4 L min^{-1} and $C_{A,feed}$ = 2.3 mol L^{-1}. The problem also specifies that the rate expression is equation (3).

$$r = kC_A^2 \tag{3}$$

According to the late-mixing segregated flow model, the conversion in this reactor can be found using equation (4).

$$\overline{f}_A = \int_{t'=0}^{t'=\infty} f_A(t') \left.\frac{dF(\lambda)}{d\lambda}\right|_{\lambda=t'} dt' \tag{4}$$

In order to utilize equation (4), we need an expression for the conversion in a fluid element as a function of residence time and an expression for the age distribution function. The latter can be found by taking the derivative of equation (2), as shown in equation (5).

$$\frac{dF(\lambda)}{d\lambda} = 0.16\exp(-0.16\lambda) \tag{5}$$

Before the age distribution function shown in equation (5) is used to compute the conversion, one should check that it is properly normalized. If the age function is properly normalized, integration of the age distribution function over all possible values of the age should yield a value of 1, as equation (6) indicates. Evaluating the integral in equation (6) numerically shows that it is, indeed, equal to 1.

$$\int_{t'=0}^{t'=\infty} \left.\frac{dF(\lambda)}{d\lambda}\right|_{\lambda=t'} dt' = \int_0^\infty 0.16\exp(-0.16t')dt' = 1 \tag{6}$$

To generate an expression for the conversion in a fluid element as a function of residence time we model the fluid element as a perfectly mixed batch reactor initially containing reactant A at a concentration of 2.3 mol L^{-1}, that is at the feed concentration. Treating it as a batch reactor, the mole balance design equation for a fluid element is given by equation (7). The variables in equation (7) can be separated and the equation can be integrated from time zero, where the moles of A will equal $VC_{A,feed}$ to some arbitrary time, t', equation (8). Upon integration of equation (8) an expression for the moles of A at any given time is obtained, equation (9). Substitution of equation (9) into the definition of fractional conversion yields the desired expression for the conversion in a fluid element as a function of residence time, equation (10).

$$\frac{dn_A}{dt} = -kVC_A^2 = -kV\left(\frac{n_A}{V}\right)^2 \tag{7}$$

$$-\int_{VC_{A,feed}}^{n_A(t')} \frac{dn_A}{n_A^2} = \frac{k}{V}\int_0^{t'} dt \tag{8}$$

$$n_A(t') = \frac{VC_{A,feed}}{1 + kt'C_{A,feed}} \tag{9}$$

$$f_A(t') = \frac{VC_{A,feed} - n_A(t')}{VC_{A,feed}} = \frac{kt'C_{A,feed}}{1 + kt'C_{A,feed}} \tag{10}$$

Substitution of equations (5) and (10) into the late-mixing segregated flow model, equation (4), yields equation (11). Evaluating the integral in equation (11) numerically, one finds that the conversion is 75.5%.

$$\overline{f}_A = \int_{t'=0}^{t'=\infty} \left(\frac{kt'C_{A,feed}}{1 + kt'C_{A,feed}}\right)\left(0.16\exp(-0.16t')\right)dt' \tag{11}$$

An astute reader of this example may have noticed that the age function given in equation (2) is actually the age function for an ideal CSTR with a volume of 25 L and an inlet flow rate of 4 L min^{-1}.

However, if the reactor in this example is modeled as an ideal CSTR, one finds the conversion to equal 69%, not 75.5%. In other words, using the ideal CSTR age function in the segregated flow model gives a different conversion than using the ideal CSTR model. The reason for this can be understood qualitatively by consideration of the macro-mixing for the two models. In the CSTR there is complete macro-mixing at all times, whereas in the segregated flow model, macro-mixing only occurs at the end of the process. When the reaction kinetics are first order, this difference in macro-mixing has no effect, and the CSTR model predicts the same conversion as the late-mixing segregated flow model using an ideal CSTR age distribution function. For any other kinetics, however, the two models predict different conversions.

Calculation Details Using MATLAB

The calculations for this problem are quite straightforward, simply involving the numerical integration of two functions between specified limits of zero and infinity. With some software, one would need to pick a large value to use in place of infinity, but in MATLAB one can, in fact, specify infinity as one of the limits of integration. MATLAB provides a built-in function, `integrate`, to perform the integration. It takes three arguments, the first is a function which computes the integrand and the other two are the upper and lower integration limits. The only thing one must be aware of is that the function one provides to compute the integrand will be passed a vector as its argument. Therefore, within the function one must be careful to use the proper multiplication and division symbols depending whether vector multiplication/division is desired or element by element multiplication/division.

With that caveat, the MATLAB function used to perform the calculations is shown in Listing 1. It begins by defining the known constants, after which two functions are defined. the first, `agefun`, calculates the integrand in equation (6), and the other, `sfmfun`, calculates the integrand in equation (11). The last two lines evaluate the integrals according to those equations, displaying the results in the MATLAB workspace.

```
% MATLAB file used in the solution of Example 36.1 of "A First Course on
% Kinetics and Reaction Engineering."
function Example_36_1
    % Known constants
    k = 0.5; % L/mol/min
    V = 25.; % L
    Vdot = 4.; % L/min
    CAfeed = 2.3; % mol/L

    % Define the functions to be integrated numerically
    agefun = @(x) 0.16*exp(-0.16*x);
    sfmfun = @(x) k*CAfeed*x./(1+k*CAfeed*x)*0.16.*exp(-0.16*x);

    % Check the normalization of the age function
    age_check = integral(agefun,0,Inf)

    % Calculate the conversion using the segregated flow model
    fA_SF = integral(sfmfun,0,Inf)

end % of Example_36_1
```

Listing 1. Full listing of the MATLAB function, Example_36_1, used to perform the calculations for this example.