A First Course on Kinetics and Reaction Engineering

Example 36.2

Problem Purpose

This problem illustrates the use of the late-mixing segregated flow model to represent a non-ideal reactor with an age function generated from stimulus-response data.

Problem Statement

Example 11.3 described a 50 cm^3 stirred tank reactor with a feed flow rate of 100 cm^3 min^{-1}. In that example, the response to a step change tracer concentration stimulus was used to generate the age function data shown in the table below. Use the late-mixing segregated flow model and those age function data to determine the isothermal conversion of A in the reaction A → B. The feed concentration of A is 1.3 mol L^{-1}, and reaction is first order in A with a rate coefficient of 0.7 min^{-1}.

Residence Time (min)	***Age, F***
0	0.00
0.1	0.03
0.2	0.13
0.3	0.21
0.4	0.32
0.5	0.38
0.6	0.46
0.7	0.54
0.8	0.61
0.9	0.68
1	0.77
1.1	0.80
1.2	0.81
1.3	0.84
1.4	0.85
1.5	0.89
1.6	0.90
1.7	0.91
1.8	0.91
1.9	0.92
2	0.93

Problem Analysis

This problem tells us to model a reactor using the late-mixing segregated flow model, so the type of problem is pretty clear. In order to use the late-mixing segregated flow model we will need the age distribution function and an expression for the conversion as a function of time for a perfectly mixed fluid element. The latter can be generated by solving the batch reactor design equations and substituting the result into the definition of conversion. There are a few approaches we could take to generate the age distribution function. Here, we will use forward differences to approximate the age distribution function at each of the residence times in the table. Seeing that the age never reaches 1, it will likely be necessary to re-normalize the resulting age distribution function values. After doing that, the integral in the late-mixing segregated flow model will be evaluated numerically using the trapezoid rule.

Problem Solution

Reading through the problem statement one finds that the following quantities are specified: V = 50 cm^3, $\dot{V}$ = 100 cm^3 min^{-1}, $C_{A,feed}$ = 1.3 mol L^{-1} and k = 0.7 min^{-1}. The problem also specifies that the rate expression is equation (1).

$$r = kC_A \tag{1}$$

According to the late-mixing segregated flow model, the conversion in this reactor can be found using equation (2).

$$\overline{f}_A = \int_{t'=0}^{t'=\infty} f_A\left(t'\right)\left.\frac{dF\left(\lambda\right)}{d\lambda}\right|_{\lambda=t'} dt' \tag{2}$$

In order to utilize equation (2), we need an expression for the conversion of A in a fluid element as a function of residence time and the age distribution function. 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 the feed concentration of 1.3 mol L^{-1}. The mole balance design equation for A in a fluid element is given by equation (3). The variables in equation (3) 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 (4). Upon integration of equation (4) an expression for the moles of A at any given time is obtained, equation (5). Substitution of equation (5) into the definition of fractional conversion yields the desired expression for the conversion in a fluid element as a function of residence time, equation (6).

$$\frac{dn_A}{dt} = -kVC_A = -kV\left(\frac{n_A}{V}\right) = -kn_A \tag{3}$$

$$\int_{VC_{A,feed}}^{n_A(t')} \frac{dn_A}{n_A} = -k\int_0^{t'} dt \tag{4}$$

$$n_A\left(t'\right) = VC_{A,feed}\exp\left(-kt'\right) \tag{5}$$

$$f_A\left(t'\right) = \frac{VC_{A,feed} - n_A\left(t'\right)}{VC_{A,feed}} = 1 - \exp\left(-kt'\right) \tag{6}$$

As indicated in the problem analysis, in this problem we will use forward differences to approximate the derivative of F with respect to residence time at each of the residence times (except the last) in the data table. Equation (7) shows how the derivative is approximated. I am using $F'(i)$ here to represent the age value for data point i in the table, with the prime on the F denoting that the age function has not been properly normalized yet. Similarly, $t'(i)$ represents the residence time for data point i in the table. Using forward differences will give one less derivative value than the number of residence time values. Here, the age distribution function at the final residence time will be set equal to zero, effectively assuming that no fluid exits the reactor with an age greater than the final value in the table, 2 min.

$$\left.\frac{dF'}{dt'}\right|_{t'=t'(i)} \simeq \frac{F'\left(i+1\right) - F'\left(i\right)}{t'\left(i+1\right) - t'\left(i\right)} \tag{7}$$

If the age distribution function is properly normalized, then it's integral over all possible residence times should equal 1, as indicated in equation (8). Here it is likely that equation (8) is not obeyed and that the age distribution values calculated using equation (7) will need to be re-normalized. To do so, the integral in equation (8) is evaluated and the age distribution function is divided by the result, as indicated in equation (9), where the derivative on the left-hand side of the equals sign does not have a prime, denoting that it is properly normalized. The integral in equation (9) can be evaluated using the trapezoid rule since we have a set of values for the integrand instead of a continuous function.

$$\int\limits_{t'=0}^{t'=\infty} \left.\frac{dF\left(\lambda\right)}{d\lambda}\right|_{\lambda=t'} dt' = 1 \tag{8}$$

$$\left.\frac{dF}{dt'}\right|_{t'=t'(i)} = \frac{\left.\dfrac{dF'}{dt'}\right|_{t'=t'(i)}}{\displaystyle\int\limits_{t'=0}^{t'=\infty} \left.\frac{dF'\left(\lambda\right)}{d\lambda}\right|_{\lambda=t'} dt'} \tag{9}$$

Indeed, upon evaluation, the integral in equation (8) is found to equal 0.915, so the approximate derivatives computed using equation (7) are each divided by 0.915 to obtain properly normalized values of the age distribution function. To check the normalization, the integral in equation (8) is evaluated using the re-normalized age distribution function values, and as expected, it does equal 1.

At this point, all that remains is to substitute the age distribution function and the conversion as a function of residence time into equation (2), leading to equation (10), and then to calculate the conversion using equation (10). In this problem, the integral in equation (10) is again evaluated using the trapezoid rule since we have discrete values of the age distribution function and not a continuous analytical function.

$$\overline{f}_A = \int_{t'=0}^{t'=\infty} \left(1 - \exp\left(-kt'\right)\right) \left.\frac{dF(\lambda)}{d\lambda}\right|_{\lambda=t'} dt' \tag{10}$$

Numerical solution of equation (10) shows that according to the late-mixing segregated flow model, the conversion is 32.7%.

Calculation Details Using MATLAB

The calculations for this problem are not complicated. They make use of two built-in MATLAB functions. The first, `diff`, computes the differences between the elements of a vector, and the second, `trapz`, numerically integrates x-y data using the trapezoid rule. The MATLAB documentation can be consulted if you have questions about how to call and use these functions. If you don't know how numerical integration is performed using the trapezoid rule, you should consult a good introductory calculus textbook.

A MATLAB function named Example_36_2 was created to perform the calculations for this problem; it is shown in its entirety in Listing 1. It begins with the entry of the known constants specified in the problem statement, after which the residence times and the age function values from the data table are entered as column vectors.

Values of the non-normalized age distribution function are next calculated according to equation (7). This is where the built-in function, `diff`, is used. Actually is it used twice, once to calculate the differences between the F' values (the numerator in equation (7)) and once to calculate the differences between the t' values (the denominator in equation (7)). The results from `diff` are vectors, so it is important to use element-by-element division (./), and not vector division (/), when calculating the approximate derivatives. Of course, the number of derivatives is one less than the number of ages or residence times, because when you get to the last entry in the table, there isn't a next value to use to calculate a forward difference. I made the assumption that none of the fluid that leaves the reactor has an age greater than the last residence time in the data table, and accordingly, I set the value of the age distribution function for the last point equal to zero.

Since the age data are experimental, it is quite likely that they are not properly normalized. Therefore, the necessary normalization factor is calculated by evaluating the integral in equation (8) using the trapezoid rule. The properly normalized age distribution function is then calculated by dividing the non-normalized values by this normalization factor. The normalization is then checked by again evaluating the integral in equation (8), where it is now expected that the value will equal 1.

The last few lines of code calculate the integrand in equation (10) and then solve equation (10) using the trapezoid rule.

```
% MATLAB file used in the solution of Example 36.2 of "A First Course on
% Kinetics and Reaction Engineering."
function Example_36_2
    % Known constants
    V = 50.; % cm^3
    Vdot = 100.; % cm^3/min
    CAfeed = 1.3/1000; % mol/cm^3
    k = 0.7; % /min

    % Given age data
    lambda = [0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1; 1.1;
        1.2; 1.3; 1.4; 1.5; 1.6; 1.7; 1.8; 1.9; 2];
    Fprime = [0.00; 0.03; 0.13; 0.21; 0.32; 0.38; 0.46; 0.54; 0.61; 0.68;
        0.77; 0.80; 0.81; 0.84; 0.85; 0.89; 0.90; 0.91; 0.91; 0.92; 0.93];

    % Approximate dFprime/dt, equation (7)
    dFprime_dt = diff(Fprime)./diff(lambda);
    % Set dFprime/dt equal to zero for the last residence time
    dFprime_dt = [
        dFprime_dt
        0
    ];

    % Calculate the normalization factor using the integral in equation (8)
    norm = trapz(lambda,dFprime_dt)
    dFdt = dFprime_dt/norm;
    % Calculate the re-normalized age distribution function using the
    % integral in equation (8)
    check = trapz(lambda,dFdt)

    % Use the late-mixing segregated flow model, equation (10), to
    % calculate the conversion
    integrand = zeros(length(lambda),1);
    for i=1:length(lambda)
        integrand(i) = (1-exp(-k*lambda(i))).*dFdt(i);
    end
    fA = trapz(lambda,integrand)

end % of Example_36_2.m
```

Listing 1. Full listing of the MATLAB function, Example_36_2, used to perform the calculations for this problem.