

A First Course on Kinetics and Reaction Engineering

Example 32.1

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It illustrates the analysis of a semi-batch reactor where one species is being added to the reactor during processing.

Problem Statement*

The hydrolysis of acetic anhydride, reaction (1), can run away thermally in a batch reactor [1], but this can be prevented using semi-batch operation [2]. Suppose the rate can be described using a rate expression that is first order in acetic anhydride with a pre-exponential factor of $1.192 \times 10^{15} \text{ min}^{-1}$ and an activation energy of $97,600 \text{ J mol}^{-1}$. The heat of reaction may be taken to be constant and equal to $-58,615 \text{ J mol}^{-1}$. The reacting fluid in the semi-batch reactor for the process is cooled by an external fluid uniformly maintained at $60 \text{ }^\circ\text{C}$; the product of the heat transfer area and the heat transfer coefficient, UA , equals $260 \text{ cal min}^{-1} \text{ K}^{-1}$. The reactor operates at atmospheric pressure and initially contains 67 cm^3 of water, 283 cm^3 of acetic acid (the solvent and product) and 0.30 cm^3 of sulfuric acid at $60 \text{ }^\circ\text{C}$. The heat capacity of the fluid in the reactor may be taken to be constant and equal to $2.68 \text{ J cm}^{-3} \text{ K}^{-1}$. Acetic anhydride at $21 \text{ }^\circ\text{C}$ is fed to the reactor at a rate of $64.5 \text{ cm}^3 \text{ min}^{-1}$ for the first 5.5 minutes of operation, after which the reaction continues in batch mode. The solution may be assumed to be ideal with a constant density. Plot (a) the temperature of the fluid in the reactor and (b) the concentration of acetic anhydride in the reactor as a function of processing time.



Problem Analysis

The rate expression for the reaction is known and the problem asks questions related to reactor performance. Hence, this is a reaction engineering problem. The problem describes semi-batch operation of a reactor wherein one reagent is added to the batch reactor over time. Thus, to answer the questions posed, semi-batch mole and energy balances will be formulated and solved. As described in the problem statement, the semi-batch processing is immediately followed by a second stage of continued batch processing. In principal this means that the semi-batch design equations must be used to analyze the first stage of processing, and then the results must be used as the initial conditions for the subsequent batch processing. It will be found, however, that for this particular problem, the semi-batch design equations can

* This problem is loosely based upon the work of Haldar and Rao [1,2], but the rate expression was modified and additional assumptions regarding fluid and reactor properties were introduced. This was done to avoid intricate details from obscuring the basic approach to the analysis of a semi-batch reactor. Therefore, the results presented here should not be used for engineering purposes, but rather the original work should be consulted.

be solved for the entire processing time, provided that the inlet flow terms are set equal to zero when semi-batch processing ends and batch processing commences.

Problem Solution

To simplify the notation, let A represent acetic anhydride, B represent water and Z represent acetic acid, in which case the reaction is given by equation (2).



To begin the analysis, we read through the problem statement and each time a quantity is encountered, it is assigned to the appropriate variable. Doing this leads to the following specifications: $k_0 = 1.192 \times 10^{15} \text{ min}^{-1}$, $E = 97,600 \text{ J mol}^{-1}$, $\Delta H(T) = -58,615 \text{ J mol}^{-1}$, $T_e = 60 \text{ }^\circ\text{C}$, $UA = 260 \text{ cal min}^{-1} \text{ K}^{-1}$, $P = 1 \text{ atm}$, $V_{A,0} = 0 \text{ cm}^3$, $V_{B,0} = 67 \text{ cm}^3$, $V_{Z,0} = 283 \text{ cm}^3$, $V_{cat,0} = 0.30 \text{ cm}^3$, $T_0 = 60 \text{ }^\circ\text{C}$, $\tilde{C}_p = 2.68 \text{ J cm}^{-3} \text{ K}^{-1}$, $T_{stream} = 21 \text{ }^\circ\text{C}$, $\dot{V}_A = 64.5 \text{ cm}^3 \text{ min}^{-1}$, $t_{semi} = 5.5 \text{ min}$. The problem states that the liquid is ideal and has constant density, so the initial volume of fluid in the reactor is given by equation (3).

$$V_0 = V_{A,0} + V_{B,0} + V_{Z,0} + V_{cat,0} \quad (3)$$

The general form of the semi-batch reactor mole balance design equation is given in equation (4), and the general form of the energy balance design equation is given in equation (5). Mole balances can be written for each of the reagents, A, B and Z. In this problem, there is only one reaction taking place, so the summations over j reduce to a single term. If the work done by the agitator is neglected, there is no work being done by shafts or moving boundaries, and since the pressure is specified as being constant, its derivative with respect to time will equal zero. Hence two terms in equation (5) will equal zero. The only reagent flowing into the reactor is A, so \dot{n}_B and \dot{n}_Z are equal to zero. Finally, the volumetric heat capacity for the fluid as a whole is given, so the summation of the individual molar flow rates times the molar heat capacities can be replaced by the product of the volumetric heat capacity of the fluid as a whole multiplied by the fluid volume. Making all these substitutions and writing the equations in the standard form with a derivative on one side of the equals sign and the rest of the equation on the other side leads to the design equations given in equations (6) through (9). There are four design equations, t is the independent variable and n_A , n_B , n_Z and T are the dependent variables, as the equations indicate.

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j \quad (4)$$

$$\begin{aligned} \dot{Q} - \dot{W} &= \sum_{\substack{i=all \\ species}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,stream}) \\ &+ \frac{dT}{dt} \sum_{\substack{i=all \\ species}} (n_i \hat{C}_{pi}) + V \sum_{\substack{j=all \\ reactions}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt} \end{aligned} \quad (5)$$

$$\frac{dn_A}{dt} = f_1(t, n_A, n_B, n_Z, T) = \dot{n}_A - Vr \quad (6)$$

$$\frac{dn_B}{dt} = f_2(t, n_A, n_B, n_Z, T) = -Vr \quad (7)$$

$$\frac{dn_Z}{dt} = f_3(t, n_A, n_B, n_Z, T) = 2Vr \quad (8)$$

$$\frac{dT}{dt} = f_4(t, n_A, n_B, n_Z, T) = \frac{-Vr\Delta H + P\frac{dV}{dt} - \dot{n}_A(\hat{h}_A - \hat{h}_{A,stream}) + \dot{Q}}{V\tilde{C}_p} \quad (9)$$

Looking more closely at equations (6) through (9), it can be seen that if \dot{n}_A and the derivative of the reaction volume with respect to time are both set equal to zero, the resulting equations are the batch reactor design equations for this system. Therefore, this one set of design equations can be used for all stages of processing provided that the values of \dot{n}_A and the derivative of the reaction volume with respect to time are both set equal to zero at the time when reactant addition ceases, t_{semi} . Notice also that the reaction volume, V , will be increasing up to that point, after which it will become constant.

The semi-batch reactor design equations are initial value ordinary differential equations, and they can be solved numerically. In order to do so, no matter what software is used, it will be necessary to provide (a) initial values of the independent and dependent variables (in this case the initial values are the values at the start of processing), (b) the final value of either the independent variable or one of the dependent variables, and (c) code that is given values for the independent and dependent variables and that uses those values to evaluate and return the corresponding values of the functions f_1 through f_4 in equations (6) through (9).

Some students get confused when specifying the initial values for a semi-batch reactor. Remember, it is the initial values of the independent and dependent variables that are specified. The independent variable is the time, and defining t to equal zero at the start of processing is the standard practice. The dependent variables in equations (6) through (9) are n_A , n_B , n_Z and T . Their values at the start of processing (i. e. at $t = 0$) are the necessary initial values. In this problem, there is no A present in the reactor at the start of processing, so the initial value of n_A is zero, equation (10). Students sometimes get confused and use the inlet molar flow rate of A, \dot{n}_A , as the initial value, but this is wrong. The dependent variable is n_A , the moles of A in the reactor, not the molar flow rate of A into the reactor. We are not told the initial moles of B and Z, but we are told their volumes. The initial moles can be found from that information using equations (10) and (11), but in order to use those equations we will need to look up the densities, ρ_i , and molecular weights, M_i , of those two species in handbooks or other reliable sources. The last dependent variable is the temperature of the reacting fluid, T , and the problem specifies the initial temperature of the fluid in the reactor, T_0 , so the necessary initial condition for temperature is given by equation (13).

$$n_A(t=0) = 0 \quad (10)$$

$$n_B(t=0) = \frac{\rho_B V_{B,0}}{M_B} \quad (11)$$

$$n_Z(t=0) = \frac{\rho_Z V_{Z,0}}{M_Z} \quad (12)$$

$$T(t=0) = T_0 \quad (13)$$

The problem does not state the final value of the processing time or any of the dependent variables. Instead, it asks for plots as a function of processing time. To generate a single point for a plot, one would choose a value for the final time, solve the design equations and use the results to calculate the quantities to be plotted. This would then be repeated many times to create a set of points which could then be used to make the plot. When the equations are solved numerically, the software used often automates the process of generating the points and making the plots.

The last thing that must be provided in order to solve the design equations is code that is given values for the independent and dependent variables, t , n_A , n_B , n_Z and T , and that uses them to evaluate the functions f_1 through f_4 in equations (6) through (9). Upon examining those functions, one learns that they contain the following quantities whose values are not given in the problem statement: \dot{n}_A , V , r , $\frac{dV}{dt}$,

\hat{h}_A , \hat{h}_{stream} and \dot{Q} . In order to evaluate the functions, f_1 through f_4 , it will be necessary to calculate values for these quantities using the values of the independent and dependent variables passed to the code, the quantities given in the problem statement and additional quantities found in handbooks or other reference sources.

The inlet molar flow rate of A is not specified, but its inlet volumetric flow rate, \dot{V} , is. The density and molecular weight of A can be looked up in a handbook or other reference source. Reagent A only flows into the reactor during the semi-batch operation, and the duration of semi-batch operation, t_{semi} , is specified. Hence, up to this time, the molar flow rate of A into the process is given by equation (14); after that the inlet flow rate is zero, equation (15).

$$\dot{n}_A = \frac{\dot{V} \rho_A}{M_A}; (t \leq t_{semi}) \quad (14)$$

$$\dot{n}_A = 0; (t > t_{semi}) \quad (15)$$

The reaction volume will be changing during semi-batch operation because fluid is being added. The initial volume can be calculated from the specified initial volumes of B, Z and catalyst, equation (16), since the liquids are assumed to be ideal. In addition, the inlet flow rate is constant, so the volume can be

calculated at any time during semi-batch processing using equation (17). After semi-batch processing ends, the volume will remain constant at its final value, equation (18).

$$V^0 = V_B^0 + V_Z^0 + V_{cat}^0 \quad (16)$$

$$V = V^0 + \dot{V}t ; (t \leq t_{semi}) \quad (17)$$

$$V = V^0 + \dot{V}t_{semi} ; (t > t_{semi}) \quad (18)$$

The problem specifies that the rate is first order in A and it provides values for the pre-exponential factor and the activation energy. Hence, the rate can be calculated using equation (19), but in order to do so, the concentration of A is needed. By definition, the concentration is given by equation (20). The moles of A will be given to the code, and the volume will be calculated as just described, after which the rate can be computed.

$$r = k_0 \exp\left(\frac{-E}{RT}\right) C_A \quad (19)$$

$$C_A = \frac{n_A}{V} \quad (20)$$

The derivative of the reaction volume with respect to time is found simply by differentiating equations (17) and (18), leading to equations (21) and (22).

$$\frac{dV}{dt} = \dot{V} ; (t \leq t_{semi}) \quad (21)$$

$$\frac{dV}{dt} = 0 ; (t > t_{semi}) \quad (22)$$

The term $\dot{n}_A (\hat{h}_A - \hat{h}_{A,stream})$ represents the difference in the enthalpy of the feed stream at the feed stream conditions and its enthalpy at reaction conditions. In this problem, the feed stream is a liquid and it remains a liquid at reaction conditions. The only change is in its temperature, and so, this term is a sensible heat. It can be calculated using equation (23).

$$\dot{n}_A (\hat{h}_A - \hat{h}_{A,stream}) = \dot{n}_A \hat{C}_{p,A} (T - T_{stream}) \quad (23)$$

Finally, the problem specifies the product of the heat transfer coefficient and the heat transfer area, UA , and it specifies the temperature of the coolant, T_e , so the heat input term can be calculated using equation (24).

$$\dot{Q} = UA(T_e - T) \quad (24)$$

At this point the design equations can be solved numerically. Doing so, as described earlier, will yield the values of the moles of A, B and Z in the reactor and the reaction temperature as a function of time. The latter can be used to generate the first requested plot, Figure 1.

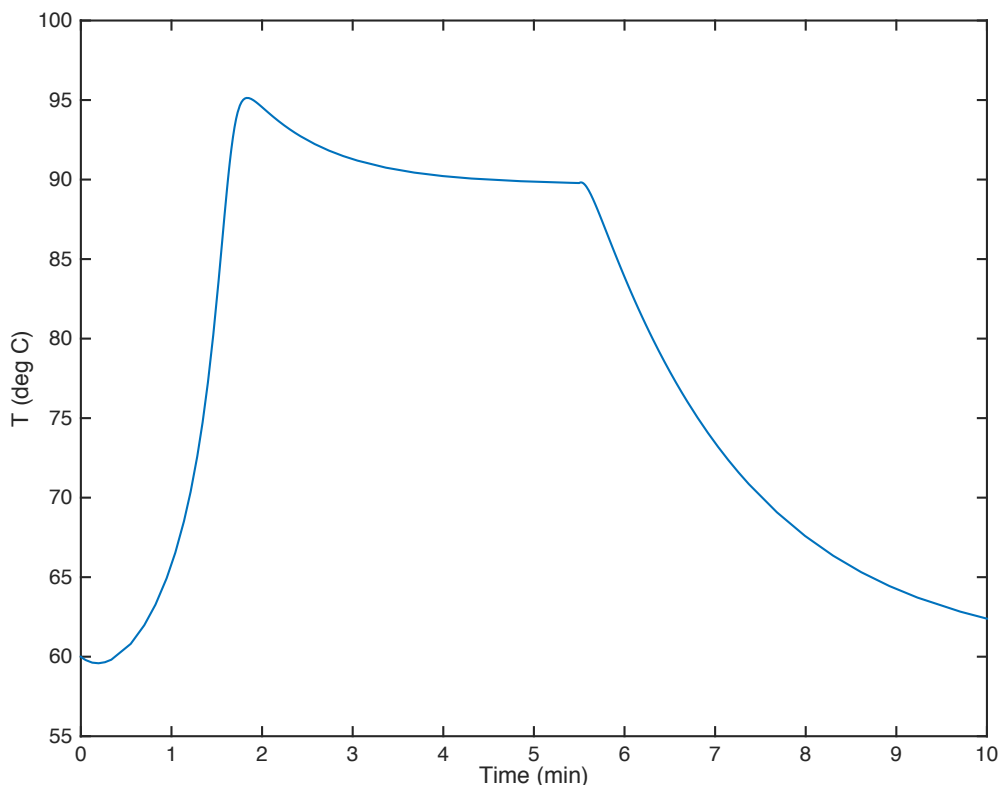


Figure 1. Temperature as a function of processing time.

The concentration of A as a function of processing time can be computed using equation (20) with the reaction volume computed using equation (17) or (18), as appropriate. The results can then be used to generate the second requested plot, Figure 2.

The results shown in Figures 1 and 2 make sense on physical grounds. Initially, as A is added, it causes the reaction temperature to drop because it is colder than the reactor contents, and upon being added, it is diluted to a low concentration so that the reaction rate is small, releasing little heat of reaction. As more A is added, the rate increases, and this releases heat causing the temperature to rise at a rate that is controlled by the rate at which A is added. When the addition of A ceases at 5.5 min, the temperature can be seen to drop more rapidly since the heat evolved by reaction quickly becomes negligible due to consumption of all of the A.

If all of the A were added at the start and the reactor was operated in batch mode, the initial concentration of A would be 5.34 mol/L compared to a maximum concentration of less than 1.2 mol/L during semi-batch processing. That higher concentration would cause a very large initial rate, leading to a very rapid temperature rise. The available cooling might not be able to control the rapid temperature rise, leading to vaporization of the the fluid from the reactor. This could pose serious safety threats. Semi-batch operation allows the temperature rise to be controlled, thereby preventing excessive temperature rise.

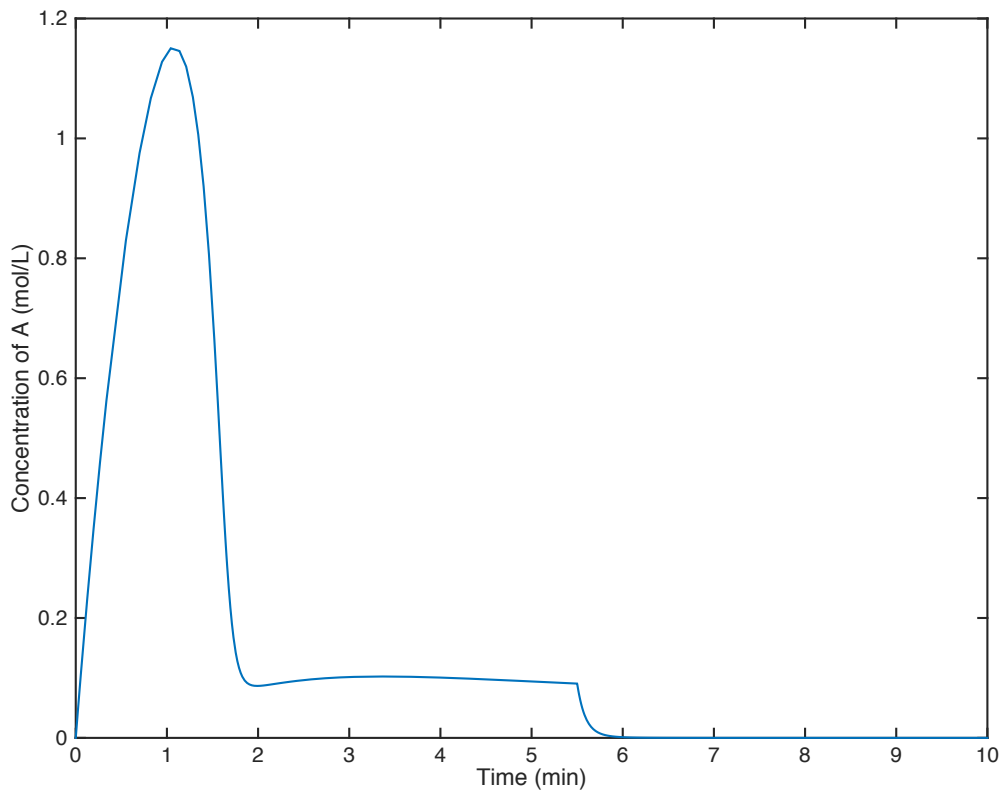


Figure 2. Concentration of A as a function of processing time.

Calculation Details Using MATLAB

The design equations for this problem, equations (6) through (9), are initial value differential equations. Solution of equations of this kind is described in Supplemental Unit S5. The final value of the independent variable can be specified for each point to be plotted, so the template file SolvIVDifl.m from Supplemental Unit S5 can be modified and used to solve the present design equations.

To do so I first changed the initial comment and the function declaration statement so that the function is named Example_32_1 and there are no return values. I then entered all the known quantities given in the problem statement along with necessary constants found in handbooks and other reference sources. Following that, additional necessary constant quantities were calculated. All quantities were entered in a consistent set of units. All of these modifications can be seen in Listing 1.

```

% Modified version of the AFCoKaRE MATLAB template file SolvIVDifD.m used
% in the solution of Example 32.1 of "A First Course on Kinetics and
% Reaction Engineering.
%
function Example_32_1
    % Known quantities and constants (in min, mol, J, K, cc, g)
    k0 = 1.192E15; % /min
    E = 97600.; % J/mol
    dH = -58615.; % J/mol
    Te = 60 + 273.15; % K
    UA = 260*4.184; % J/min/K
    VB0 = 67.0; % cc
    Vcat = 0.3; % cc
    VZ0 = 283.0; % cc
    T0 = 60 + 273.15; % K
    Cp_soln = 2.68; % J/cc/K
    Tstream = 21 + 273.15; % K
    VFR = 64.5; % cc/min
    t_semi = 5.5; % min
    Tfinal = 60 + 273.15; % K
    P = 1.0; % atm
    % Data from handbooks, etc.
    R = 8.31446; % J/mol/K
    rhoA = 1.082; % g/cc
    MWA = 102.; % g/mol
    CpA = 168.2; % J/mol/K
    rhoB = 1.0; % g/cc
    MWB = 18.; % g/mol
    rhoZ = 1.049; % g/cc
    MWZ = 60.; % g/mol
    % Calculated constants
    V0 = VB0 + VZ0 + Vcat;
    nA0 = 0;
    nB0 = VB0*rhoB/MWB;
    nZ0 = VZ0*rhoZ/MWZ;

```

Listing 1. Modified initial comment and function statement followed by entry of known constants.

The internal function `odeqns` was next modified. This internal function is passed values for the independent and dependent variables as the scalar, t , and the vector, z , respectively. Its purpose is to use these values to evaluate functions f_1 through f_4 in equations (6) through (9). It was first modified to extract the dependent variables from the vector, z . Next it was modified so the unknown quantities that appear in the functions to be evaluated were calculated using equations (14) through (24). (To keep the code a little more readable, I calculated individual terms in the energy balance separately.) The last modification to `odeqns` was to evaluate the functions f_1 through f_4 in equations (6) through (9) and save them as the elements of the vector $dzdt$, which is returned by `odeqns`. The resulting version of `odeqns` is shown in Listing 2.


```

% Function that evaluates the ODEs
function dzdt = odeqns(t,z)
    % t is the value of the independent variable
    % z is a vector containing the values of the dependent variables
    nA = z(1);
    nB = z(2);
    nZ = z(3);
    T = z(4);
    if (t > t_semi)
        ndotA = 0;
        V = V0 + VFR*t_semi;
        dVdt = 0;
    else
        ndotA = VFR*rhoA/MWA;
        V = V0 + VFR*t;
        dVdt = VFR;
    end
    CA = nA/V;
    r = k0*exp(-E/R/T)*CA;
    rxnHeat = -V*r*dH;
    sensHeat = ndotA*CpA*(T-Tstream);
    Qdot = UA*(Te-T);
    expansWork = P*dVdt*0.1013; % J/min
    netHeat = rxnHeat + expansWork - sensHeat + Qdot;
    dzdt = [
        ndotA - V*r;
        -V*r;
        2*V*r;
        (-V*r*dH + expansWork - sensHeat + Qdot)/(V*Cp_soln);
    ];
end % of internal function odeqns

```

Listing 2. Modified version of the internal function odeqns.

The third modification involved entering the initial and final values from equations (10) through (13). A final processing time of 10 min was arbitrarily chosen. If the plots had been unsatisfactory, this value would have been changed accordingly. Listing 3 shows the modifications along with the code from the original template file that solves the ODEs and extracts the final values of the independent and dependent variables. There was a possibility that these equations might be stiff since initially the amount of A was changing much more rapidly than the other dependent variables, so the ODE solver was changed from ode45 to ode15s.

```
% Initial values
t0 = 0;
z0 = [
      nA0
      nB0
      nZ0
      T0
];
tf = 10.0;

% Solve the ODEs
[t, zz] = ode15s(@odeqns,[t0, tf],z0);

% Extract the final values of the independent and dependent variables
last_value = length(t);
t_f = t(last_value); % final value of the independent variable
z = zz(last_value,:); % final values of the dependent variables
```

Listing 3. Entry of the initial and final values and solution of the ODEs.

The final modification involved calculation of the concentration of A versus time from the moles of A versus time as discussed in the solution and the generation of the requested plots. I also calculated what the initial concentration of A would have been if the reactor had been operated batch-wise. These modifications are shown in Listing 4.

```

% calculate the concentration versus time
conc_A = zeros(1,length(t));
for i=1:length(t);
    if t(i) < t_semi
        V = V0 + VFR*t(i);
    else
        V = V0 + VFR*t_semi;
    end
    conc_A(i) = zz(i,1)/V;
end
% convert to degrees C and mol/L
T_C = zz(:,4)-273.15;
conc_A = conc_A*1000.0;
% make the plots
figure
plot(t,T_C)
xlabel('Time (min)')
ylabel('T (deg C)')
figure
plot(t,conc_A)
xlabel('Time (min)')
ylabel('Concentration of A (mol/L)')

% calculate the batch-wise initial concentration of A (mol/L)
nA_batch = VFR*t_semi*rhoA/MWA;
V0_batch = V0 + VFR*t_semi;
CA_batch = nA_batch/V0_batch*1000

end % of Example_32_1.m

```

Listing 4. Calculation of the concentration and generation of the plots.

Execution of the function Example_32_1 produced the two plots shown in Figures 1 and 2 and the output shown in Listing 5.

```

>> Example_32_1

CA_batch =

    5.3374

```

Listing 5. Output generated by Example_32_1.

References Cited

- [1] R. Haldar, D.P. Rao, Chem. Eng. Technol., 15 (1992) 34-38.
- [2] R. Haldar, D.P. Rao, Chem. Eng. Technol., 15 (1992) 39-43.