Reaction Engineering Basics Example 8.4.1

Matlab Work-Up

Before summarizing the assignment, the file, `example_8_4_1.m`, was created for performing the calculations. Within it a function of the same name was declared. Each of the blocks of code listed below are added to this file to complete the function for performing the calculations.

```
function example_8_4_1()
% Calculations for Example 8.4.1 in "Reaction Engineering Basics, The Book"
```

Assignment Summary

Reaction

$$A + B \rightarrow S + W \tag{1}$$

Rate Expression

$$r_1 = k_1 C_A C_B \tag{2}$$

Reactor: Non-adiabatic, liquid-phase SBSTR

Given Constants: $C_{A,0}$ = 15 M, T_0 = 20 °C, $C_{B,in}$ = 15 M, T_{in} = 20 °C, V = 10 L, V_A = 5.0 L, $\dot{V}_{in}$ = 0.25 L min^{-1}, V_B = 5 L, V_{ex} = 2.5 L, $T_{ex,in}$ = 20 °C, $\dot{V}_{ex,in}$ = 2.5 L min^{-1}, A_{ex} = 2150 cm^2 , U = 73 cal cm^2 h^{-1} K^{-1}, $T_{ex,0}$ = 20 °C, $\tilde{C}_p = \tilde{C}_{p,ex}$ = 1 g cm^{-3}, $\rho = \rho_{ex}$ = 1 cal g^{-1} K^{-1}, ΔH_1 = –13.7 kcal mol^{-1}, $k_{0,1}$ = 8.11 x 10^{12} L mol^{-1} s^{-1}, E_1 = 17.7 kcal mol^{-1}, and P = 1 atm.

The given and known constants were converted to consistent units and addded to `example_8_4_1`.

```
% global constants available to all functions
% given
CA_0 = 15.0; % mol/L
T_0 = 20 + 273.15; % K
CB_in = 15.0; % mol/L
T_in = T_0;
V_0 = 5.0; % L
Vdot_in = 0.25/60; % L/s
V_B = 5.0; % L
V_ex = 2.5; % L
Tex_in = 20 + 273.15; % K
Vdot_ex = 2.5/60; % L/s
A = 2150; % cm^2
U = 73/60/60; % cal/cm^2/s/K
Tex_0 = 20 + 273.15; % K
rho = 1000.0; % g/L
Cp = 1.0; % cal/g/K
dH_1 = -13700.0; % cal/mol
k0_1 = 8.11E12; % L/mol/s
E_1 = 17700.0; % cal/mol
P = 1.0; % atm
% known
Re = 1.987; % cal/mol/K
Rw = 0.08206; % L-atm/mol/K
% calculated
nDotB_in = Vdot_in*CB_in;
nA_0 = CA_0*V_0;
mDot_ex = Vdot_ex*rho;
V_f = V_0 + V_B;
```

Task: Parametric analysis

- Parameter: t
- Items of Interest: C_A and T *vs.* t as graphs

Preliminary Analysis

The assignment narrative suggests that the reaction is very fast. If it is effectively instantaneous, the base will be completely converted upon addition to the reactor. In that case, the concentration of acid will decrease at essentially the same rate as the rate at which the base is

added. If the reaction is fast, but not instantaneous, the concentration of acid will decrease at a rate that is less than the rate at which the base is added.

In either case, the temperature change will be determined by the relative rates of heat generation and heat removal. Thus, even if the reaction is effectively instantaneous, the temperature of the reacting fluid will not increase linearly due to the heat removal by the cooling fluid.

SBSTR Model Function

SBSTR Design Equations

$$\frac{dn_A}{dt} = -Vr_1 \tag{3}$$

$$\frac{dn_B}{dt} = \dot{n}_{B,in} - Vr_1 \tag{4}$$

$$\frac{dn_S}{dt} = Vr_1 \tag{5}$$

$$\rho V\tilde{C}_p\frac{dT}{dt} - P\frac{dV}{dt} = \dot{Q} - \rho\dot{V}_{in}\tilde{C}_p\left(T - T_{in}\right) - Vr_1\Delta H_1 \tag{6}$$

$$\rho_{ex}V_{ex}\tilde{C}_{p,ex}\frac{dT_{ex}}{dt} = -\dot{Q} - \dot{m}_{ex}\int_{T_{ex,in}}^{T_{ex}}\tilde{C}_{p,ex}dT = -\dot{Q} - \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right) \tag{7}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{8}$$

SBSTR Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_S$, $\underline{T}$, $\underline{T}_{ex}$, and $\underline{V}$.

Additional Computable Unknowns: r_1, k_1, C_A, C_B, $\dot{n}_{B,in}$, $\dot{Q}$, and $\dot{m}_{ex}$.

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{10}$$

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{11}$$

$$\dot{n}_{B,in} = \dot{V}_{in}C_{B,in} \tag{12}$$

$$\dot{Q} = UA_{ex}\left(T_{ex} - T\right) \tag{13}$$

$$\dot{m}_{ex} = \rho \dot{V}_{ex} \tag{14}$$

IVODE Solver Requirements

1. Initial values

$$t_{iv} = 0 \tag{15}$$

$$n_{A,iv} = C_{A,0} V_A \tag{16}$$

$$n_{B,iv} = 0 \tag{17}$$

$$n_{S,iv} = 0 \tag{18}$$

$$T_{iv} = T_0 \tag{19}$$

$$T_{ex,iv} = T_{ex,0} \tag{20}$$

$$V_{iv} = V_A \tag{21}$$

2. Stopping criterion

$$V = V_f = V_A + V_B \tag{22}$$

3. SBSTR derivatives function that

   a. receives the independent and dependent variables (t, n_A, n_B, n_S, T, T_{ex}, and V) at the start of an integration step as arguments

   b. calculates the additional unknowns using equations (2) and (10) through (14)

   c. evaluates and returns the SBSTR design equation derivatives using equations (3) through (5), (8), (23), and (24).

$$\frac{dT}{dt} = \frac{\dot{Q} - \rho\dot{V}_{in}\tilde{C}_p\left(T - T_{in}\right) - Vr_1\Delta H_1 + P\dot{V}_{in}}{\rho V\tilde{C}_p} \tag{23}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex}\tilde{C}_p\left(T_{ex} - T_{ex,in}\right)}{\rho V_{ex}\tilde{C}_p} \tag{24}$$

The SBSTR model and SBSTR derivatives functions were added to `example_8_4_1`.

```
% SBSTR reactor function
function [t, nA, nB, nS, T, Tex, V] = sbstr_model_variables()
    % set the initial values
    ind_0 = 0.0;
    dep_0 = [nA_0, 0.0, 0.0, T_0, Tex_0, V_0];

    % define the stopping criterion
    stopVar = 6;
    stopVal = V_f;

    % solve the IVODEs
    odes_are_stiff = false;
    [t, dep, success, message] = solve_ivodes(ind_0, dep_0, stopVar...
        , stopVal, @sbstr_derivatives, odes_are_stiff);

    % check for solver issues
    if ~success
        disp('')
        disp(["SBSTR function issue: ", message])
        disp(' Press any key to continue or Ctrl-C to exit')
        pause
    end

    % extract the dependent variables
    nA = dep(:,1);
    nB = dep(:,2);
    nS = dep(:,3);
    T = dep(:,4);
    Tex = dep(:,5);
    V = dep(:,6);
end

% SBSTR derivatives function
```

```
function ddt = sbstr_derivatives(~, dep)
    % extract the dependent variables
    nA = dep(1);
    nB = dep(2);
    T = dep(4);
    Tex = dep(5);
    V = dep(6);

    % calculate the additional unknowns
    k_1 = k0_1*exp(-E_1/Re/T);
    CA = nA/V;
    CB = nB/V;
    r = k_1*CA*CB;
    Qdot = U*A*(Tex - T);

    % evaluate the derivatives
    dnAdt = -V*r;
    dnBdt = nDotB_in -V*r;
    dnSdt = V*r;
    dTdt = (Qdot - rho*Vdot_in*Cp*(T - T_in) - V*r*dH_1 ...
        + P*Vdot_in*Re/Rw) /(rho*V*Cp);
    dTexdt = (-Qdot - mDot_ex*Cp*(Tex - Tex_in))/(rho*V_ex*Cp);
    dVdt = Vdot_in;

    % return the derivatives as a column vector
    ddt = [dnAdt; dnBdt; dnSdt; dTdt; dTexdt; dVdt];
end
```

Items of Interest Function

1. Call the SBSTR model function to get $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_S$, $\underline{T}$, $\underline{T}_{ex}$, and $\underline{V}$.
2. Calculate $\underline{C}_A$.

$$\underline{C}_A = \frac{\underline{n}_A}{\underline{V}} \tag{25}$$

3. Convert units as desired and generate the requested graphs.

To complete `example_8_4_1`, the items of interest function was added along with a line of code to call it and perform the calculations.

```
    % items_of_interest function
    function items_of_interest()
        % solve the reactor design equations
        [t, nA, ~, ~, T, ~, V] = sbstr_model_variables();

        % calculate the items of interest for plotting and convert units
        CA = nA./V;
        T_C = T - 273.15;
        t_min = t/60;

        % tabulate, show and save the final concentration and temperature
        item = ["Final Concentration of A"; "Final Temperature"];
        value = [CA(end); T_C(end)];
        units = ["M"; "°C"];
        resultsTable = table(item, value, units);
        disp('')
        disp(resultsTable)
        disp('')
        writetable(resultsTable, 'results.csv')

        % display and save the graphs
        figure
        plot(t_min, CA, 'LineWidth', 2)
        xlabel("Time (min)", "FontSize", 14)
        ylabel("Concentration of A (mol/L)", "FontSize", 14)
        set(gca, 'FontSize', 14)
        saveas(gcf, 'CA_vs_t.png')

        figure
        plot(t_min, T_C, "LineWidth", 2)
        xlabel("Time (min)", "FontSize", 14)
        ylabel("Temperature (°C)", "FontSize", 14)
        set(gca, 'FontSize', 14)
        saveas(gcf, 'T_vs_t.png')
    end

    % perform the calculations
    items_of_interest()
end
```

Results

The calculations were performed by calling the function, `example_8_4_1`, and no solver issues were encountered.

The acid concentration as a function of reaction time is shown in Figure 1. The temperature of the reacting fluid as a function of reaction time is shown in Figure 2.

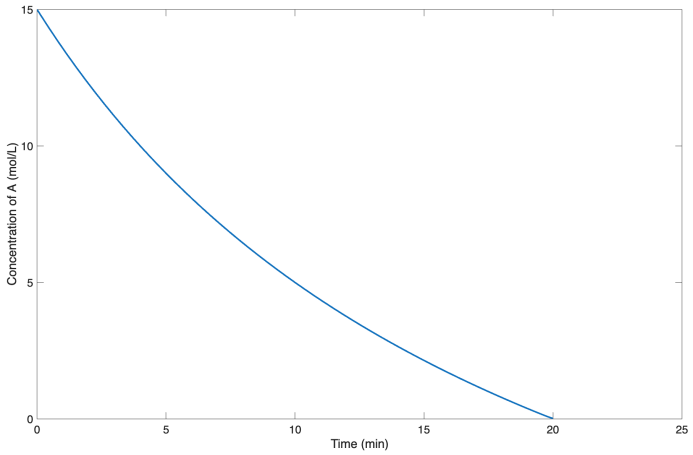


Figure 1: Concentration of acid during the additon of base to the reactor.

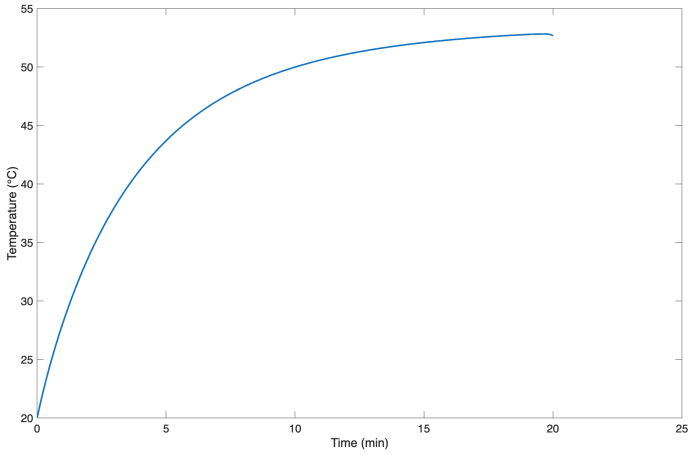


Figure 2: Reacting fluid temperature during the additon of base to the reactor.

Discussion

The rate of decrease of the acid concentration is not linear. As noted in the preliminary analysis, this suggests that while the reaction is fast, it is not instantaneous. As a consequence there are three factors affecting the instantaneous reaction rate: the concentration of acid, the concentration of base, and the temperature of the reacting fluid. The curvature in the graphs results from the effect of the concentraion of acid upon the rate.

Summary

The concentration and temperature profiles during the addition of the base to the SBSTR are shown in Figure 1 and Figure 2, respectively. At the instant the addition of the base to the reactor is completed, the concentration of acid is less than 0.02 M and the temperature of the reacting fluid is 52.7 °C