Reaction Engineering Basics Example 8.4.3

Matlab Work-Up

Before summarizing the assignment, the file, `ex_8_4_3.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 ex_8_4_3()
% Calculations for Example 8.4.3 from REB, The Book
```

Assignment Summary

Reaction

$$A + W \rightarrow 2Z \tag{1}$$

Rate Expression

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

Reactor: Non-adiabatic, liquid-phase SBSTR with a 2 stage operational protocol

Given Constants: $k_{0,1}$ = 1.192 x 10^{15} min^{-1}, E_1 = 97,600 J mol^{-1}, ΔH_1 = -58,615 J mol^{-1}, V_{ex} = 300 cm^3, $T_{ex,in}$ = 60 °C, $\dot{V}_{ex,in}$ = 250 cm^3 min^{-1} UA = 260 cal min^{-1} K^{-1}, P = 1 atm, $V_{W,0}$ = 67 cm^3 $V_{Z,0}$ = 283 cm^3, $V_{H_2SO_4,0}$ = 0.30 cm^3, T_0 = 60 °C, $T_{ex,0}$ = 60 °C, $\breve{C}_p$ = 2.68 J cm^{-3} K^{-1}, V_A = 350 cm^3, T_{in} = 21 °C, T_f = 65 °C, T_{max} = 95 °C, ρ_A = 1.082 g cm^{-3}, ρ_W = 1.0 g cm^{-3}, ρ_Z = 1.049 g cm^{-3}, M_A = 102 g mol^{-1}, M_W = 18 g mol^{-1}, M_Z = 60 g mol^{-1}, $\hat{C}_{p,A}$ = 168.2 J mol^{-1} K^{-1}, ρ_{ex} = 1.0 g cm^{-3}, and $\tilde{C}_{p,ex}$ = 1 cal g^{-1} K^{-1}.

The given and known constants are converted to consistent units and addded to `ex_8_4_3`.

```
% global constants available to all functions
% given
k0_1 = 1.192E15; % /min
E_1 = 97600; % J/mol
dH_1 =-58615; % J/mol
V_ex = 300; % cm^3
Tex_in = 60 + 273.15; % K
Vdot_ex = 250; % cm^3/min
UA = 260*4.184; % J/min/K
P = 1.0; % atm
VW_0 = 67; % cm^3
VZ_0 = 283; % cm^3
Vacid = 0.3; % cm^3
T_0 = 60 + 273.15; % K
Tex_0 = 60 + 273.15; % K
Cp = 2.68; % J/cm^3/K
V_A = 350; % cm^3
T_in = 21 + 273.15; % K
T_f = 65 + 273.15; % K
T_max = 95 + 273.15; %K
rho_A = 1.082; % g/cm^3
rho_W = 1.0; % g/cm^3
rho_Z = 1.049; % g/cm^3
M_A = 102; % g/mol
M_W = 18; % g/mol
M_Z = 60; % g/mol
Cp_A = 168.2; % J/mol/K
rho_ex = 1.0; % g/cm^3
Cp_ex = 1.0*4.184; % cal/g/K
% known
Re = 1.987*4.184; % J/mol/K
Rw = 82.06; % cm^3-atm/mol/K
% calculated
V_0 = VW_0 + VZ_0 + Vacid;
m_ex = Vdot_ex*rho_ex;
nW_0 = VW_0*rho_W/M_W;
nZ_0 = VZ_0*rho_Z*M_Z;
```

Task: Optimization

- Parameter: $\dot{V}_{A,in}$
- Minimization Target: t_f
- Constraint: $\underline{T} < T_{max}$
- Items of Interest: $\dot{V}_{A,opt}$, $f_{A,f}\big|_{\dot{V}_{opt}}$, and $\underline{T}\big|_{\dot{V}_{opt}}$ and $\underline{C}_A\big|_{\dot{V}_{opt}}$ *vs.* $\underline{t}$ as graphs.

Preliminary Analysis

By adding the reactant at a controlled rate, the amount of heat released can be controlled so that the maximum temperature the system never reaches is 95 °C. Since the rate increases with temperature, the total processing time will decrease with temperature. Consequently, the minimum reaction time will result when the maximum temperature is 95 °C.

SBSTR Model Function

SBSTR Design Equations

$$\frac{dn_A}{dt} = \dot{n}_{A,in} - Vr_1 \tag{3}$$

$$\frac{dn_W}{dt} = -Vr_1 \tag{4}$$

$$\frac{dn_Z}{dt} = 2Vr_1 \tag{5}$$

$$V\breve{C}_p\frac{dT}{dt} - P\frac{dV}{dt} = \dot{Q} - \dot{n}_{A,in}\hat{C}_{p,A}\left(T - T_{in}\right) - Vr_1\Delta H_1 \tag{6}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{n}_{A,in}\hat{C}_{p,A}\left(T - T_{in}\right) - Vr_1\Delta H_1 + P\dot{V}_{in}}{V\breve{C}_p} \tag{7}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex}V_{ex}\tilde{C}_{p,ex}} \tag{8}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{9}$$

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

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

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

$$C_A = \frac{n_A}{V} \tag{11}$$

$$\dot{Q} = UA\,(T - T_{ex}) \tag{12}$$

$$\dot{m}_{ex} = \dot{V}_{ex}\rho_{ex} \tag{13}$$

$$\dot{n}_{A,in} = \frac{\dot{V}_{in}\rho_A}{M_A} \tag{14}$$

$$\begin{aligned} \dot{V}_{in} &= \dot{V}_{A,in} \qquad \text{stage 1} \\ \dot{V}_{in} &= 0 \qquad \text{stage 1} \end{aligned} \tag{15}$$

Uncomputable Unknown (Received as an Argument): $\dot{V}_{A,in}$

The SBSTR derivatives function needs $\dot{V}_{A,in}$ (equations (7) and (9)), so the SBSTR model function must make it available as a global variable.

IVODE Solver Requirements

1. Stage 1

    a. Initial values

$$t_{iv,1} = 0 \tag{16}$$

$$n_{A,iv,1} = 0 \tag{17}$$

$$n_{i,iv,1} = n_{i,0} = \frac{V_{i,0}\rho_i}{M_i} \qquad i = W \text{ and } Z \tag{18}$$

$$T_{iv,1} = T_0 \tag{19}$$

$$T_{ex,iv,1} = T_{ex,0} \tag{20}$$

$$V_{iv,1} = V_0 = V_{W,0} + V_{Z,0} + V_{acid,0} \tag{21}$$

b. Stopping criterion

$$t = t_1 = \frac{V_A}{\dot{V}_{in}} \tag{22}$$

2. Stage 2

a. Initial values

$$t_{iv,2} = t_1 \tag{23}$$

$$n_{i,iv,2} = \underline{n}_i\big|_{t=t_1} \qquad i = A, W \text{ and } Z \tag{24}$$

$$T_{iv,2} = \underline{T}\big|_{t=t_1} \tag{25}$$

$$T_{ex,iv,2} = \underline{T}_{ex}\big|_{t=t_1} \tag{26}$$

$$V_{iv,2} = \underline{V}\big|_{t=t_1} \tag{27}$$

b. Stopping criterion

$$T = T_f \tag{28}$$

3. SBSTR derivatives function that

a. receives receives the reactor model variables (t, n_A, n_W, n_Z, T, T_{ex}, and V) at the start of an integration setp
b. can access the current value of $\dot{V}_{A,in}$
c. calculates the additional unknowns using equations (2) and (10) through (15)
d. evaluates and returns the SBSTR design equation derivatives using equations (3) through (9)

To facilitate making $\dot{V}_{A,in}$ available to the SBSTR derivatives function, the global variable, `g_Vdot_in` is declared and set to `nan` initially. Then the SBSTR model and derivatives functions are added to `ex_8_4_3`.

```
% global variable for the current inlet volumetric flow rate
g_Vdot_in = nan;

% SBSTR reactor function
function [t, nA, nW, nZ, T, Tex, V] = sbstr_model_variables(Vdot_in)
    % set the current value of the inlet volumetric flow rate
    g_Vdot_in = Vdot_in;

    % set the initial values for the first stage
    ind_0 = 0.0;
    dep_0 = [0.0, nW_0, nZ_0, T_0, Tex_0, V_0];
```

```
% set the stopping criterion for the first stage
t_1 = V_A/Vdot_in;
stopVar = 0;
stopVal = t_1;

% solve the design equations for the first stage
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 model first stage issue: ", message])
    disp('Press any key to continue or CTRL-C to exit')
    pause
end

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

% repeat for the second stage
g_Vdot_in = 0;
ind_0 = t(end);
dep_0 = [dep(end,1), dep(end,2), dep(end,3), dep(end,4), dep(end,5)...
    , dep(end,6)];
stopVar = 4;
stopVal = T_f;
[t2, dep2, success, message] = solve_ivodes(ind_0, dep_0, stopVar...
    , stopVal, @sbstr_derivatives, odes_are_stiff);
if ~success
    disp('')
    disp(["SBSTR model second stage issue: ", message])
    disp('Press any key to continue or CTRL-C to exit')
    pause
end
```

```
        % combine the results for the two stages
        t = [t; t2];
        nA = [nA; dep2(:,1)];
        nW = [nW; dep2(:,2)];
        nZ = [nZ; dep2(:,3)];
        T = [T; dep2(:,4)];
        Tex = [Tex; dep2(:,5)];
        V = [V; dep2(:,6)];
    end

    % SBSTR derivatives function
    function ddt = sbstr_derivatives(~, dep)
        % extract the dependent variables
        nA = dep(1);
        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;
        r_1 = k_1*CA;
        Qdot = UA*(Tex-T);
        nA_in = g_Vdot_in*rho_A/M_A;

        % evaluate the derivatives
        dnAdt = nA_in - V*r_1;
        dnWdt = - V*r_1;
        dnZdt = V*r_1;
        dTdt = (Qdot - nA_in*Cp_A*(T - T_in) - V*r_1*dH_1 ...
                + P*g_Vdot_in*Re/Rw)/(Cp*V);
        dTexdt = (-Qdot - m_ex*Cp_ex*(Tex-Tex_in))/(rho_ex*V_ex*Cp_ex);
        dVdt = g_Vdot_in;

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

Coupled Unknowns Residuals Function

As noted in the preliminary analysis, the optimum inlet volumetric flow rate will result in a maximum temperature that just equals the specified value of $T_{max} = 95$ °C. This can be expressed in the form of the implicit residual expression shown in equation (29).

$$\dot{V}_{A,in} \; : \; \max\left(\underline{T}\right) = T_{max} \quad \Rightarrow \quad 0 = \max\left(\underline{T}\right) - T_{max} = \epsilon \tag{29}$$

Coupled Unknown Residual Function

1. receives a guess for the coupled unknown, $\dot{V}_{A,in}$, as an argument
2. calls the SBSTR model function using the guess as the argument to get $\underline{t}$, $\underline{n}_A$, $\underline{n}_W$, $\underline{n}_Z$, $\underline{T}$, $\underline{T}_{ex}$, and $\underline{V}$
3. calculates additional unknowns using equations (2), and (10) through (15)
4. evaluates and returns coupled unknown residual using equation (29)

The coupled unknowns residuals function is added to `ex_8_4_3` next.

```
% coupled unknown residual function
function epsilon = coupled_unknown_residual(guess)
    % solve the SBSTR design equations using the guess
    [~, ~, ~, ~, T, ~, ~] = sbstr_model_variables(guess);

    % evaluate and return the residual
    epsilon = max(T) - T_max;
end
```

Items of Interest Function

1. Define a guess for the optimum feed rate
2. Call an ATE solver passing that guess and the coupled unknown residual function to get $\dot{V}_{A,in,opt}$
3. Call the SBSTR model function passing that value to get $\underline{t}$, $\underline{n}_A$, $\underline{n}_W$, $\underline{n}_Z$, $\underline{T}$, $\underline{T}_{ex}$, and $\underline{V}$
4. Calculate the final conversion

$$f_A = \frac{V_A \rho_A M_A - \underline{n}_A\big|_{t_f}}{V_A \rho_A M_A} \tag{30}$$

5. Calculate the concentration of acetic acid during processing

$$\underline{C}_A = \frac{\underline{n}_A}{\underline{V}} \tag{31}$$

6. Generate the graphs and present the results

To complete `ex_8_4_3`, 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
    % define a guess for the volumetric feed rate
    VdotGuess = 35;

    % solve the implicit equation for the Vdot_opt
    [soln, success, message] = solve_ates(@coupled_unknown_residual...
        , VdotGuess);

    % check for solver issues
    if ~success
        disp('')
        disp("Coupled unknown solver issue: ")
        disp(message)
        disp('Press any key to continue or CTRL-C to exit')
        pause
    end

    % extract the result
    Vdot_opt = soln(1);

    % solve the reactor design equations using the optimum feed rate
    [t, nA, ~, ~, T, ~, V] = sbstr_model_variables(Vdot_opt);

    % calculate the conversion
    f_A = 100*(V_A*rho_A/M_A - nA(end))/(V_A*rho_A/M_A);

    % tabulate, show and save the results
    item = ["Optimum Feed Rate"; "Processing Time"...
        ; "Acetic Anhydride Conversion"];
    value = [Vdot_opt; t(end); f_A];
    units = ["cm^3^ min^-1^"; "min"; "%"];
    resultsTable = table(item, value, units);
    disp('')
    disp(resultsTable)
    disp('')
    writetable(resultsTable, 'ex_8_4_3_results.csv')
```

```
    % Generate plot data
    CA = nA./V;

    % generate graphs
    figure
    plot(t, T - 273.15, 'LineWidth', 2)
    xlabel("Processing Time (min)", "FontSize", 16)
    ylabel("Reacting Fluid Temperature (°C)", "FontSize", 16)
    yline(T_max - 273.15, ':r', 'LineWidth', 2)
    set(gca,'FontSize', 16)
    saveas(gcf,'ex_8_4_3_T_vs_t.png')

    figure
    plot(t, CA, 'LineWidth', 2)
    xlabel("Processing Time (min)", "FontSize", 16)
    ylabel("Acetic Acid Concentration (mol cm^-^3)", "FontSize", 16)
    set(gca,'FontSize', 16)
    saveas(gcf,'ex_8_4_3_CA_vs_t.png')

    % as a check, calculate the maximum temperature and processing time for
    % volumetric flows slightly smaller and larger than the optimum

    Vdot = [0.95*Vdot_opt; 1.05*Vdot_opt];
    Tmax = [nan; nan];
    tproc = [nan; nan];

    for i = 1:2
        [t, ~, ~, ~, T, ~, ~] = sbstr_model_variables(Vdot(i));
        tproc(i) = t(end);
        Tmax(i) = max(T) - 273.15;
    end

    % tabulate, show, and save the results
    checkTable = table(Vdot, Tmax, tproc);
    checkTable.Properties.VariableNames = ["Feed Rate (cm^3 min^-1)"...
        ,"Maximum Temperature (°C)", "Processing Time (min)"];
    disp('')
    disp(checkTable)
    disp('')
    writetable(checkTable, 'ex_8_4_3_check.csv')
end
```

```
    % perform the calculations
    items_of_interest()
end
```

Results

The calculations were performed by calling the function, `ex_8_4_3`.

```
>> ex_8_4_3
                item                    value          units
    ----------------------------    ------    ---------------

    "Optimum Feed Rate"              39.481    "cm^3^ min^-1^"
    "Processing Time"                17.015    "min"
    "Acetic Anhydride Conversion"       100    "%"
```

The acetic anhydride concentration profile is shown in Figure 1, and the temperature profile is shown in Figure 2. A feed rate of 39.5 cm^3 min^{-1} results in the minimum processing time, 17 min, that meets the temperature constraint. At the end of processing, the conversion of acetic anhydride is 100%.

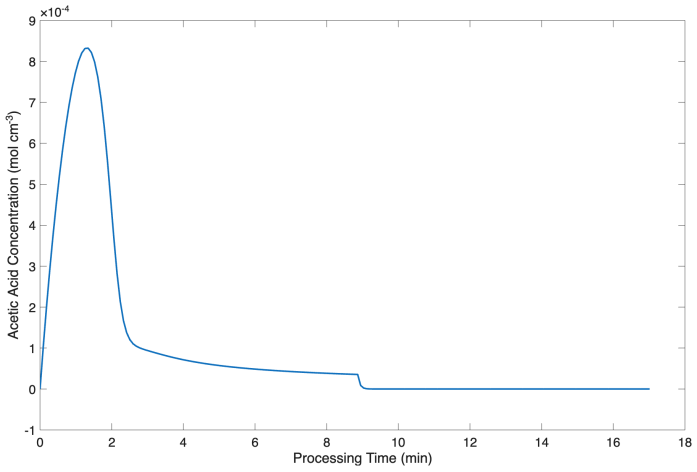


Figure 1: Profile of acetic acid concentration in the optimized SBSTR

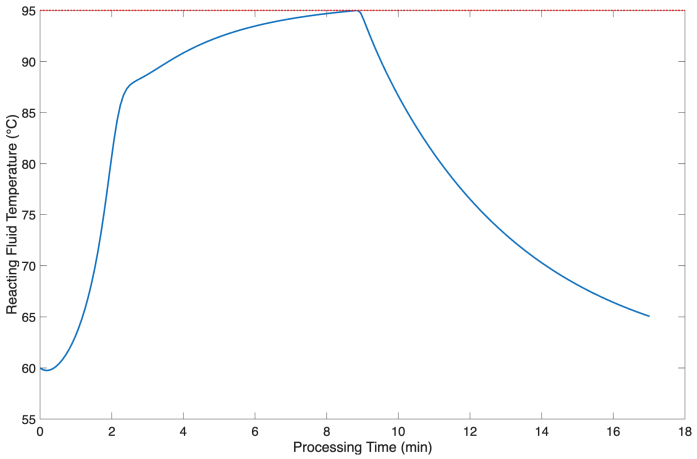


Figure 2: Temperature profile in the optimized SBSTR

Discussion

The shapes of the profiles are consistent with a qualitative analysis of the process. During semi-batch processing two factors are at work with respect to the reactant concentration and three factors are at work with respect to the temperature. The flow into the reactor tends to increase the reactant concentration while the reaction tends to decrease it. Figure 1 shows that the concentration rises steadily until it passes through a maximum. Prior to the maximum, the feed is adding A faster than the reaction is consuming it. After the maximum, the opposite is true. Of course increasing the concentration tends to increase the rate and decreasing it tends to decrease the rate. Once the feed stops, at 9 min, the concentration quickly drops to zero.

As for temperature, the cold feed and the cooling water remove heat and tend to lower the temperature while the reaction releases the heat of reaction. Figure 2 shows that initially the temperature drops very slightly. This is a result of the cold feed; heat generation is negligible because the reactant concentration is near zero making the rate very small. As the concentration of A increases the rate increases, which, in turn, increases the amount of heat being released in the system. At about the point where the concentration reaches its maximum, the temperature rise slows. This occurs because the decreasing concentration reduces the rate thereby lowering the heat being released by the reaction. Finally, at 9 min, after all of the A has been added, the rate goes to zero and heat is no longer being released into the system. From that point forward, the temperature drops as heat is removed by the cooling water.

To check that the minimum processing time results when the maximum reacting fluid temperature equals the specified limit of 95 °C, the reactor was analyzed using a slightly lower feed rate and a slightly larger feed rate. Decreasing the feed rate results in a longer processing time. Increasing the feed rate decreases the processing time, but the temperature exceeds 95 °C.

Summary

A volumetric feed rate of 39 cm^3 min^{-1} yields the smallest processing time (9 min) that satisfies the maximum temperature constraint. With that feed rate, 100% of the acetic anhydride is converted. The acetic acid concentration and temperature profiles for that volumetric feed rate are shown in Figure 1 and Figure 2.