Chapter 13: Computer Simulations and Experiments

P13-1B Review the example problems in this chapter and use a software package such as Polymath, Wolfram, or MATLAB to carry out a parameter sensitivity analysis to answer the following “What if...” questions.

What if...

(a) Example 13-1: LEP Batch Reactor

Wolfram

(i) Adiabatic Case: Use Wolfram to see if you can find a trajectory that is ready “to ignite” and whose trajectory looks like a “cobra” ready to strike, J. Vary T_0 to learn the point at which the reaction runs away at 2500 s.

(ii) Heat Exchange Case: (1) Vary sliders to try to find a “cobra-like” trajectory, J. Vary T_0 to learn the point at which the reaction runs away at 1500 s, he exit conversion as a function of T_0. (2) Use the plot of Q_g and Q_w as a function of time to describe and explain what you see as you vary T_0, N_{A0}, and m_e from their maximum to minimum values. (3) Vary some of the other parameters and identify three things you find interesting and write a conclusion.

(iii) Write a conclusion on what you found in experiments (i) and (ii).

Polymath

(iii) Modify the Polymath code so that the ambient temperature, T_a, is not constant and the coolant flow rate is 100 kg/s and with a heat capacity of 4.18 J/g. Vary the coolant flow rate and describe how the temperature and conversion trajectories change.

(iv) Modify the Polymath code to learn how your answers would change for the adiabatic case if the heat of the mixing had been neglected.

(v) How much time would it take to achieve 90% conversion for adiabatic operation if the reaction started at a very cold day where the initial temperature was 20°F? (Methanol won’t freeze at this temperature.)

(vi) Now, consider that a heat exchanger is added to the reactor for the propylene oxide reaction; the parameters are: \(C_{A0} = 1 \text{ lb-mol ft}^3, V = 1.2 \text{ ft}^3, (\Sigma N_{C_P} = 403 \text{ Btu R})\), neglect \(\Delta_{vap} U_A = 0.22 \text{ Btu}^\circ R/s, \) and \(T_0 = 498 \text{ K}.\) Plot and analyze the trajectories \(X, T, Q_g,\) and \(Q_w\) as a function of time.

(b) Example 13-2: Safety in Chemical Plants with a Runaway Reaction

Wolfram

(i) Use Wolfram to find a value of \(N_{A0}\) below which no explosion would occur when all other variables remain as in the base case. Repeat for \(N_{g0}.

(ii) Use Wolfram to find the value of \(N_{C_P}\) above which no explosion would occur.

(iii) Use Wolfram to find the value of \(U_A\) above which no explosion would occur.

Polymath

(iv) Modify the Polymath code to show that no explosion would have occurred if the cooling was not shut off for the 9.04-kmol charge of ONCB, or if the cooling was shut off for 10 min after 45 min of operation for the 3.17-kmol ONCB charge.

(v) Modify the Polymath code to show that if the cooling had been shut off for 10 min after 12 h of operation, no explosion would have occurred for the 9.04-kmol charge.

(vi) Develop a set of guidelines as to when the reaction should be quenched should the cooling fail. Perhaps safe operation could be discussed using a plot of the time after the reaction began at which the cooling failed, \(t_p\), versus the length of the cooling failure period, \(t_f\), for the different charges of ONCB.

(vii) Find a set of parameter values that would cause the explosion to occur at exactly 12:18 A.M. For example, include the mass and heat capacities of the metal reactor and/or make a new estimate of \(U_A\).

(viii) Finally, what if a 1/2-in. rupture disk rated at 800 psi had been installed and did indeed rupture at 800 psi (270°C)? Would the explosion still have occurred? Note: The mass flow rate \(\dot{m}\) varies with the cross-sectional area of the disk. Consequently, for the conditions of the reaction, the maximum mass flow rate out of the 1/2-in. disk can be found by comparing it with the mass flow rate of 830 kg/min of the 2-in. disk. Go to the Living Example Problems on the Web site and explore on your own the ONCB explosion described in Example 13-2. Explain what you would do to prevent an explosion of this type from ever occurring again while still operating at the triple production specified by management.
(c) Example 13-3: LEP CSTR Startup

**Wolfram**

(i) What is the minimum coolant flow such that there is no upturn in temperature–concentration profile for Case 2 ($T_i = 339$ K, $C_{AI} = 0$)?

(ii) Is it possible to prevent crossing of practical stability limit for Case 3 ($T_i = 344$ K, $C_{AI} = 2.26$) by varying coolant temperature, coolant flow, or overall heat transfer coefficient within reasonable limit? If so, which is the parameter and which should be varied to achieve that?

(iii) Use Wolfram to find initial temperatures and concentrations that will cause the temperature trajectory to exceed the practical stability limit, and then write a conclusion.

**Polymath**

(iv) Consider the case when $C_{AO} = 0.1$ lb mol/ft³ and $T_i = 150$°F. What is the minimum coolant temperature such that the practical stability limit is not exceeded?

(v) Describe what happens to the trajectories for an entering temperature of 70°F, an initial reactor temperature of 160°F, and an initial concentration of propylene oxide of 0.1 M.

(vi) Try various combinations of $T_{in}$, $T_i$, and $C_{AO}$ and report your results in terms of temperature–time trajectories and temperature–concentration phase planes.

(vii) Find a set of conditions above which the practical stability limit will be reached or exceeded, and those conditions below which it will not.

(viii) Vary the coolant flow rate and compare with the base case given in Figures E13-3.1 to E13-3.4. Describe what you find and then write a conclusion.

**COMSOL CSTR Startup Part 2**

(ix) Vary the tank volume between 1 m³ and 5 m³ and describe the differences in the trajectories and the time to reach steady state and exceeding a practical stability limit of 360 K.

(x) Use the base case parameters for the trajectory $T_i = 340$ K and $C_i = 1400$ mol/m³ to find the maximum feed temperature you can have that will not exceed the practical stability limit of 360 K.

(xi) Pick two operating parameters from $u_0$, $V_{tank}$, $T_{in}$, $T_{w}$, $m$, and $UA$ to vary from minimum to maximum values, and describe what you find. You will know when the maximum or minimum value has been exceeded because an error message will be displayed.

(xii) Vary the activation energy, $E_A$, between 40,000 J/mol and 120,000 J/mol and discuss the effect of $E_A$ on the number of oscillations to reach steady state.

(d) Example 13-4: LEP Semibatch

**Wolfram**

(i) Use Wolfram to vary $C_{in}$ and describe how the maximum in $C_C$ varies.

(ii) List the slider variables that have virtually no effect on the temperature trajectory. Repeat for the concentration trajectory.

(iii) Which parameter, when varied, causes the graphs of $T$ and $T_2$ to overlap each other?

(iv) What is the minimum inlet temperature such that 100% conversion of $A$ is still achieved?

**Polymath**

(v) At what times will the number of moles of $C$ ($N_C = C_C V$) and the concentration of species $C$ reach a maximum?

(vi) Are the times in part (i) that these maximums occur different, and if so, why? What would the $X$ versus $t$ and $T$ versus $t$ trajectories look like if the coolant rate were increased by a factor of 10? Why is the reaction time (252s) so short?

(vii) Problem. Assume the surface area contacting the reacting fluid changes with time. The initial fluid volume in the reactor is 0.2 m³ and the inlet volumetric flow rate is 0.004 m³/s. Calculate the heat exchanger area as a function of time if the half-pipe jacket on page *** is 0.5 m in diameter. Repeat for diameters of 1.0 m and 0.25 m.

(e) Example 13-5: LEP Multiple Reactions in a Semibatch Reactor

**Wolfram**

(i) Assume a secondary reaction ignites when the reactor temperature reaches 450K. Find the value (or combination thereof) of $C_{AO}$ and $u_0$ above which the secondary reaction will ignite.

(ii) Vary $C_{AO}$ and $u_0$ between their maximum and minimum values and describe how the concentration trajectories change and why they change the way they do.

(iii) Which parameter, when varied, results in equal concentration of $A$, $B$, and $C$ at some point in time? What is the parameter value?
Polymath
(v) At what times will the number of moles of C (N_C = C_C V) and the concentration of species C reach a maximum?
(vi) Are the times in part (i) that these maximums occur different, and if so, why? What would the X versus t and T versus t trajectories look like if the coolant rate were increased by a factor of 10? Why is the reaction time (252 s) so short?
(vii) Problem. Assume the surface area contacting the reacting fluid changes with time. The initial fluid volume in the reactor is 0.2 m^3 and the inlet volumetric flow rate is 0.004 m^3/s. Calculate the heat exchanger area as a function of time if the half-pipe jacket on page *** is 0.5 m in diameter. Repeat for diameters of 1.0 m and 0.25 m.
(e) Example 13-5: LEP Multiple Reactions in a Semibatch Reactor
Wolfram
(i) Assume a secondary reaction ignites when the reactor temperature reaches 450 K. Find the value (or combination thereof) of C_0 and v_0 above which the secondary reaction will ignite.
(ii) Vary C_0 and v_0 between their maximum and minimum values and describe how the concentration trajectories change and why they change the way they do.
(iii) Which parameter, when varied, results in equal concentration of A, B, and C at some point in time? What is the parameter value?
Polymath
(iv) Vary the volumetric flow rate between 2 < v_0 < 1,000 and compare with the base case. Describe any trends you find.
(v) Plot and analyze the trajectories of N_A = C_A V and N_B = C_B V for long times (e.g., t = 15 h). What do you observe?
(vi) Can you show for long times that N_A \approx C_0 v_0/k_{1A} and N_B \approx C_0 v_0/2k_{2B}?
(vii) What do you think is happening to this semibatch reactor if it has no lid and a maximum volume of 1,000 dm^3 at long times?
(viii) If species B is the desired product, how would you maximize N_B?
(f) Example 13-6: LEP T2 Laboratories Explosion
Wolfram
(i) Vary the liquid volume, V_0, and learn its effect on pressure profile. What is the critical value of v_0 at which pressure shoots up?
(ii) Which parameter will you vary such that concentration of B is always higher than concentration of C?
(iii) Vary different parameters and check if it is possible that the temperature limitation is reached before the pressure limitation.
(iv) Find a value of the heat of reaction for the secondary reaction of diglyme, below which no explosion would have occurred, and then write a conclusion.
Polymath
(v) View the Chemical Safety Board (CSB) video online and read the supporting reports (http://www.chemicalsafety.gov/videoroom/detail.aspx?VID=32). Also search the Web for "T2 explosion video."
(vi) (a) What did you learn from watching the video? (b) Suggest how this reactor system should be modified and/or operated in order to eliminate any possibility of an explosion. (c) Would you use backup cooling and, if so, how? (d) How could you learn if a second reaction could be set in at a higher temperature? Hint: See PRS R13.1 The Complete ARSST.
(vii) Download the Living Example Polymath E13-6. Plot C_A, C_B, C_C, P, and T as a function of time. Vary UA between 0.0 and 2.77 \times 10^6 J/h/K to find the lowest value of UA that you observe a runaway to find the value of UA below which you would observe runaway. Describe the trends as you approach runaway. Did it occur over a very narrow range of UA values? Hint: The problem becomes very stiff near the explosion condition when T > 600 K or P > 45 atm. If the temperature or pressure reaches these values, set all derivatives (concentration changes, temperature change, and pressure change) and reaction rates equal to zero so that the numerical solution will complete the analysis and hold all variables at the explosion point of the reactor.
(viii) Now let's consider the actual operation in more detail. The reactor contents are heated from 300 K to 422 K at a rate of Q = 4 K/minute. At 422 K, the reaction rate is sufficient such that heating is turned off. The reactor temperature continues to rise because the reaction is exothermic, and, when the temperature reaches 455 K, the cooling water turns on and cooling is initiated. Model this situation for the case when UA = 2.77 \times 10^6 J/h/K and when UA = 0. 
(ix) What is the maximum time in minutes that the cooling can be lost (UA = 0) starting at the time when the reactor temperature reaches 455 K so that the reactor will not reach the explosion point? The conditions are those of part (1) of this problem.
(x) Vary the parameters and operating conditions and describe what you find.
(g) LEP R13.2 Example CD13.3-5. Download the Living Example Problem for Falling Off the Upper Steady State. Try varying the entering temperature, $T_{in}$, between 80°F and 68°F, and plot the steady-state conversion as a function of $T_{in}$. Vary the coolant rate between 10,000 and 400 mol/h. Plot conversion and reactor temperature as a function of coolant rate.

(h) LEP R13.3 Example CD13.2. Download the Living Example Problem. Vary the gain, $k_c$, between 0.1 and 500 for the integral controller of the CSTR. Is there a lower value of $k_c$ that will cause the reactor to fall to the lower steady state or an upper value to cause it to become unstable? What would happen if $T_{in}$ were to fall to 65°F or 60°F?

(i) LEP R13.3 Example CD13.3. Download the Living Example Problem. Learn the effects of the parameters $k_c$ and $\tau_c$. Which combination of parameter values generates the least and greatest oscillations in temperature? Which values of $k_c$ and $\tau_c$ return the reaction to steady state the quickest?

(j) SACHE. Go to the SACHE Web site (www.sache.org). On the left-hand menu, select “SACHE Products.” Select the “All” tab and go to the module entitled: “Safety, Health and the Environment (S, H & E).” The problems are for KINETICS (i.e., CRE). There are some example problems marked K and explanations in each of the above S, H & E selections. Solutions to the problems are in a different section of the site. Specifically look at: Loss of Cooling Water (K-1), Runaway Reactions (HT-1), Design of Relief Values (D-2), Temperature Control and Runaway (K-4) and (K-5), and Runaway and the Critical Temperature Region (K-7). Go through the K problems and write a paragraph on what you have learned. Your instructor or department chair should have the username and password to enter the SACHE Web site in order to obtain the module with the problems.