NUMERICAL PROBLEM SOLVING USING MATHCAD

## in Undergraduate Reaction Engineering

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With the development and availability of fast, efficient computers, the role of computing in analysis and solution of engineering problems and graphical communication of results has increased dramatically—leading to greater need for computer-application skills in the curricula and practice of various engineering disciplines.[1] Efficient solution of problems is essential for enhanced understanding of chemical engineering principles at all course levels.[1] Commercially available computational packages, such as Maple, Mathcad, Mathematica, and Matlab, have considerably reduced the time and effort required for engineering calculations. Such programs allow engineers with limited or no formal training in programming to solve relatively complex problems.[2-4]

One of these packages, Mathcad, combines some of the best features of spreadsheets and symbolic math programs, allows efficient manipulation of large data arrays, and provides a good graphical user interface.[2, 4, 5] Ability to perform calculations with units is an important feature of Mathcad for engineering students.[2] While students need to understand the problem they are trying to solve, they may know little or nothing about numerical analysis; Mathcad allows them to work on problems even if they know very little of the program's syntax.[4] Some of the advanced and special capabilities of Mathcad, such as solution of stiff differential equations, statistical methods for nonlinear parameter estimation, and programming, have been used in undergraduate courses.[3, 5-8]

Experience in using Mathcad in the undergraduate chemical reaction engineering course at the Illinois Institute of Technology (IIT) is discussed here. Pertinent illustrations are provided to demonstrate the ease with which problems with varying complexity can be solved using Mathcad. Example problems considered for illustration deal with simultaneous solution of: linear algebraic equations (*i.e.*, kinetic parameter estimation); nonlinear algebraic equations (*i.e.*, equilibrium calculations for multiple reactions and steady-state behavior of isothermal/nonisothermal CSTR with single/multiple reactions); integral equations (*i.e.*, design of steady-state plug flow reactor, or PFR); integral-algebraic equations; and nonlinear ordinary differential equations (*i.e.*, solution of conservation equations for steady-state PFR and unsteady state CSTR). Based on these illustrations, the benefits of this user-friendly software in accelerating learning and strengthening the fundamental knowledge base should be evident. With hand calculations being replaced by computation, it is more impor-

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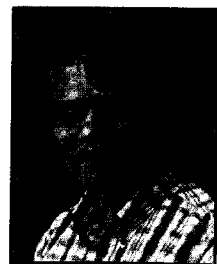
tant than ever to consistently validate and verify the results.[9] This is done, where appropriate, in the illustrations that follow. The Mathcad worksheet for each illustration is provided in a table and contains problem input, solution algorithm, and presentation of results in appropriate (numerical and/or graphical) format.

NUMERICAL ILLUSTRATIONS

Illustration 1

This illustration pertains to estimation of kinetic parameters using linear regression, which requires solution of several simultaneous equations that are linear in unknown parameters.

Consider the following relation among variables y and x_j (j = 1, 2, . . . , m) that is linear in terms of the unknown parameters θ_j (j = 1, 2, . . . , m).

$$y = y_p + e, \quad y_p = x_1\theta_1 + x_2\theta_2 + \ldots + x_m\theta_m \quad (1)$$

Information on y and x_j (j = 1, 2, . . . , m) is available in the form of n samples (n > m). The parameter estimation

problem then involves finding the parameter set

$$\hat{\Theta}\left(\theta_j = \hat{\theta}_j, j = 1, 2, \ldots, m\right)$$

for which $\sum_{i=1}^{n} e_i^2$ is minimized. After some algebra, the necessary and sufficient condition for this can be deduced to be

$$A\hat{\Theta} = b, \quad A = X^T X, \quad b = X^T Y \Rightarrow \hat{\Theta} = \left(X^T X\right)^{-1} X^T Y \quad (2)$$

with

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, \quad X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1m} \\ x_{21} & x_{22} & \cdots & x_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nm} \end{bmatrix}, \quad \Theta = \begin{bmatrix} \theta_1 \\ \theta_2 \\ \vdots \\ \theta_m \end{bmatrix} \quad (3)$$

Each column in array X represents the collection of values of a particular variable x_j (j = 1, 2, . . . ,m) for different samples. The goodness of fit of the least squares can be examined by calculating the relative error for each data point or sample (ϵ_i) defined as $\epsilon_i = (y_i - y_{ip})/y_i$, i = 1, 2, . . . , n.

The specific example considered here pertains to Problem 5-13 of Fogler[10] and involves a three-dimensional linear fit (m = 3). The dependence of the rate r of a solid-catalyzed association reaction between A and B on partial pressures of A and B, p_A and p_B, respectively, is expressed as $r = k p_A^\alpha p_B^\beta$ with k, α, and β being the kinetic parameters to be estimated. The units for k, p_A, p_B, and r are mmol/{g cat.h.(atm)$^{(\alpha+\beta)}$}, atm, atm, and mmol/{g cat.h}, respectively. Upon linear transformation of the expression, a relation linear in terms of three unknown parameters can be obtained as in Eq. (1), with $x_1 = 1$, $x_2 = \ln(p_A)$, $x_3 = \ln(p_B)$, y $= \ln(r)$, $\theta_1 = \ln(k)$, $\theta_2 = \alpha$, and $\theta_3 = \beta$. The data for p_A, p_B, and r are listed in Table 1, where the Mathcad worksheet for this problem is also shown.

Mathcad allows input only of column vectors. Two-dimensional arrays can be constructed from column vectors already introduced using the "stack" feature. The predicted reaction rates, r_p, are compared with the reaction rates available from measurements, r, and provide a very close fit (Table 1). The reason for presenting the relevant equations in this and other illustrations, where necessary, is to enable the reader to see how the equations to be solved and the Mathcad syntax are almost identical.[4] In the illustrations that follow, the subscript 0 denotes variable values at the start of a batch reactor or in the feed for a flow reactor.

Illustration 2

This illustration pertains to an autocatalytic reaction and involves comparison of space times (τ) required for steady-state isothermal operations of a CSTR and a PFR. The reaction $A + B \rightarrow 2B$ occurs as per the kinetics $r = kC_A C_B$.

TABLE 1
Worksheet for Illustration 1

$$r := \begin{pmatrix} 0.42 \\ 0.96 \\ 0.18 \\ 0.78 \\ 1.2 \\ 0.28 \\ 2.88 \end{pmatrix} \quad p_A := \begin{pmatrix} 0.1 \\ 0.2 \\ 0.05 \\ 0.3 \\ 0.4 \\ 0.05 \\ 0.5 \end{pmatrix} \quad p_B := \begin{pmatrix} 0.1 \\ 0.2 \\ 0.05 \\ 0.01 \\ 0.02 \\ 0.4 \\ 0.5 \end{pmatrix} \quad X_1 := \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

$$X_2 := \ln(p_A) \quad X_3 := \ln(p_B) \quad Y := \ln(r) \quad Q := \text{stack}\left(X_1^T, X_2^T, X_3^T\right)$$

$$X := Q^T \qquad \theta := \left(X^T \cdot X\right)^{-1} \cdot X^T \cdot Y$$

$$k := \exp(\theta_1) \qquad \alpha := \theta_2 \quad \beta := \theta_3 \quad r_p := \exp(\theta_1 \cdot X_1 + \theta_2 \cdot X_2 + \theta_3 \cdot X_3)$$

$$k = 6.652 \quad \alpha = 0.997 \quad \beta = 0.205$$

$$\overrightarrow{\frac{(r - r_p)}{r}} = \begin{pmatrix} 4.871 \times 10^{-3} \\ -1.481 \times 10^{-3} \\ -9.417 \times 10^{-3} \\ 1.073 \times 10^{-3} \\ 2.959 \times 10^{-3} \\ 6.006 \times 10^{-3} \\ -4.098 \times 10^{-3} \end{pmatrix}$$

The feed contains A and B in the ratio 100:1. For the feed composition under consideration, the reaction rate is expressed as

$$r = kC_{A0}^2 f(X), \quad f(X) = (1-X)(0.01+X) \tag{4}$$

A comparison of the required space times for a CSTR and a PFR is equivalent to the comparison of the corresponding Damkohler numbers, Da ($= kC_{A0}\tau$) which can be obtained explicitly in terms of the exit conversion X_e. The Mathcad worksheet for this problem is shown in Table 2. Rather than calculating Da for one value of X_e at a time, the Da's for CSTR and PFR are expressed as a function of X_e, a floating variable (Table 2). The Da's for a particular X_e are then readily obtained by plugging the value of X_e into the symbolic solutions. Keeping X_e floating also enables the student to represent the results graphically over a specified range of X_e ($0 < X_e < 1$ in Table 2). This beneficial feature in Mathcad is also used in Illustrations 7 and 8. For minimizing the required space time, a CSTR is the reactor of choice up to a critical conversion, X_c, and a PFR beyond this conversion (Table 2). Identifying X_c requires solution of an integral-algebraic equation in X_c—the numerical solution of which is certainly challenging for an undergraduate student. Using Mathcad, the solution is obtained rather easily and its accuracy is demonstrated in Table 2.

Illustration 3

The gas phase reaction, $SO_2 (A) + \frac{1}{2}O_2 (B) \rightarrow SO_3 (C)$, occurs as per the kinetics $r = kC_A C_B$. For the feed composition under consideration, the reaction rate is expressed as[10]

$$r = kC_{A0}^2 f(X), \quad f(X) = \frac{(1-X)(0.54-0.5X)}{(1-0.14X)^2} \tag{5}$$

with k being the kinetic coefficient, C_{A0} the feed concentration of A, and X the fractional conversion of A. The reaction is carried out in three CSTRs of equal volume in series with the exit conversion being specified. Computation of the intermediate fractional conversions and the required total space time, or of the corresponding Da $(= kC_{A0}\tau)$, requires simultaneous solution of design equations for the three reactors, viz.,

$$X_i - X_{(i-1)} - \frac{Da}{3} f(X_i) = 0, \quad i = 1, 2, 3 \tag{6}$$

In the above, X_i refers to fractional conversion of A in reactor i ($X_0 = 0$) and Da corresponds to the total space time for the three-reactor battery. The Mathcad worksheet for this problem is shown in Table 3. The solution proceeds by providing initial guesses for Da, X_1, and X_2. The validity of the solution is verified by substituting Da, X_1, and X_2 generated by the solution into Eq. (6).

TABLE 2
Worksheet for Illustration 2

$$Da_{PFR}(X_e) := \int_0^{X_e} \frac{1}{(1-X)\cdot(0.01+X)} dX$$

$$Da_{CSTR}(X_e) := \frac{X_e}{(1-X_e)\cdot(0.01+X_e)}$$
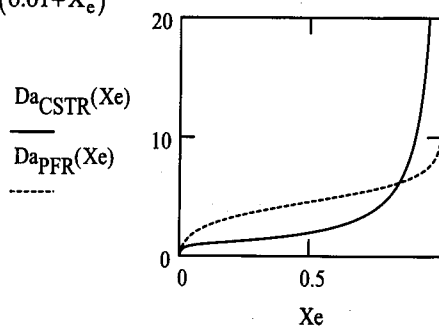
When is $Da_{CSTR} = Da_{PFR}$?

$X_e := 0.7$

Given

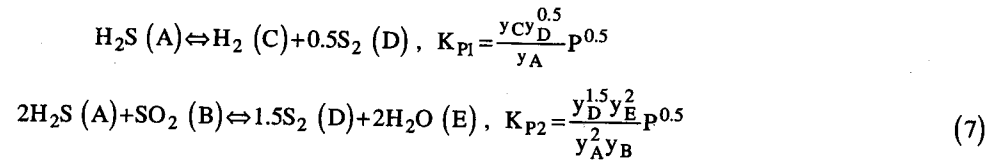$$\int_0^{X_e} \frac{1}{(1-X)\cdot(0.01+X)} dX - \frac{X_e}{(1-X_e)\cdot(0.01+X_e)} = 0$$

$X_c := Find(X_e) \quad X_c = 0.841 \quad Da_{CSTR}(X_c) = 6.222$

Verify

$$\int_0^{X_c} \frac{1}{(1-X)\cdot(0.01+X)} dX - \frac{X_c}{(1-X_c)\cdot(0.01+X_c)} = -4.187 \times 10^{-8}$$

Illustration 4

This illustration pertains to estimation of the equilibrium composition of a reaction mixture and is adopted from Problem 4.14 of Cutlip and Shacham.[11] The reactions

$$H_2S\ (A) \Leftrightarrow H_2\ (C) + 0.5S_2\ (D)\ ,\quad K_{P1} = \frac{y_C y_D^{0.5}}{y_A} P^{0.5}$$

$$2H_2S\ (A) + SO_2\ (B) \Leftrightarrow 1.5S_2\ (D) + 2H_2O\ (E)\ ,\quad K_{P2} = \frac{y_D^{1.5} y_E^2}{y_A^2 y_B} P^{0.5} \tag{7}$$

occur in a gas phase batch reactor. In the above, K_{P1} and K_{P2} denote the equilibrium coefficients, P the total pressure, and y_J the mole fraction of species J. The initial pressure P_0 is 1.2 atm and the initial composition is (I = inerts): $y_{A0} = 0.45$, $y_{B0} = 0.25$, and $y_{I0} = 0.3$. For $K_{P1} = 0.45$ atm$^{0.5}$ and $K_{P2} = 28.5$ atm$^{0.5}$, obtain the composition of the reaction mixture at equilibrium in constant volume and constant pressure operations of the reactor. Let n_{J0} denote the initial number of moles of species J, while ξ_1 and ξ_2 equal the extents of reactions 1 and 2, respectively, and n_J equals the number of moles of J after certain extents of the two reactions. The expressions for y_J's in terms of ξ_1 and ξ_2 then, are: $y_J = n_J/n_t$, $n_t = \sum_J n_J$, $n_{t0} = \sum_J n_{J0}$, and $J = A, B, C, D, E, I$, with $n_A = (n_{A0} - \xi_1 - 2\xi_2)$, $n_B = (n_{B0} - \xi_2)$, $n_C = (n_{C0} + \xi_1)$, $n_D = (n_{D0} + 0.5\xi_1 + 1.5\xi_2)$, $n_E = (n_{E0} + 2\xi_2)$, $n_I = n_{I0}$, and $n_t = (n_{t0} + 0.5\xi_1 + 0.5\xi_2)$. The mole fractions in the equilibrium relations in Eq. (7) and the reactor pressure for constant volume operation are then expressed as

$$y_A = \frac{(y_{A0} - \rho_1 - 2\rho_2)}{\psi},\quad y_B = \frac{(y_{B0} - \rho_2)}{\psi},\quad y_C = \frac{\rho_1}{\psi},\quad y_D = \frac{(0.5\rho_1 + 1.5\rho_2)}{\psi},$$

$$y_E = \frac{2\rho_2}{\psi},\quad \psi = (1 + 0.5\rho_1 + 0.5\rho_2),\quad \rho_1 = \frac{\xi_1}{n_{t0}},\quad \rho_2 = \frac{\xi_2}{n_{t0}},$$

$$P = P_0\Psi\ (\text{constant volume}),\quad P = P_0\ (\text{constant pressure}) \tag{8}$$

TABLE 3
Worksheet for Illustration 3

$$X_3 := 0.9 \quad Da := 2 \quad X_1 := 0.3 \quad X_2 := 0.6$$

Given

$$\left[X_1 - \frac{Da}{3} \cdot \frac{(1 - X_1) \cdot (0.54 - 0.5 X_1)}{(1 - 0.14 \cdot X_1)^2} \right] = 0 \qquad \left[X_2 - X_1 - \frac{Da}{3} \cdot \frac{(1 - X_2) \cdot (0.54 - 0.5 X_2)}{(1 - 0.14 \cdot X_2)^2} \right] = 0$$

$$\left[X_3 - X_2 - \frac{Da}{3} \cdot \frac{(1 - X_3) \cdot (0.54 - 0.5 X_3)}{(1 - 0.14 \cdot X_3)^2} \right] = 0 \qquad \begin{pmatrix} Da \\ X_1 \\ X_2 \end{pmatrix} := Find(Da, X_1, X_2)$$

$$Da = 19.502 \quad X_1 = 0.635 \quad X_2 = 0.823$$

Verify

$$\left[X_1 - \frac{Da}{3} \cdot \frac{(1 - X_1) \cdot (0.54 - 0.5 X_1)}{(1 - 0.14 \cdot X_1)^2} \right] = -9.212 \times 10^{-9}$$

$$\left[X_2 - X_1 - \frac{Da}{3} \cdot \frac{(1 - X_2) \cdot (0.54 - 0.5 X_2)}{(1 - 0.14 \cdot X_2)^2} \right] = -3.984 \times 10^{-9}$$

$$\left[X_3 - X_2 - \frac{Da}{3} \cdot \frac{(1 - X_3) \cdot (0.54 - 0.5 X_3)}{(1 - 0.14 \cdot X_3)^2} \right] = 0$$

The Mathcad worksheet for constant volume operation is shown in Table 4. The equilibrium relations are nonlinear coupled equations in the dimensionless extents, ρ_1 and ρ_2, initial guesses for which need to be supplied (Table 4). The extents calculated are substituted into equilibrium relations to verify that these indeed are satisfied. Computations for constant pressure operation, not shown here, proceed in a similar fashion. Illustration 4 reveals to the students the uniqueness of the physically realizable equilibrium composition for a given initial composition.

Illustration 5

Illustration 5 pertains to multiplicity of steady states in an isothermal CSTR. The reaction under consideration, catalytic hydrogenation of olefins, obeys the kinetics $r = C_A/(1+C_A)^2$, with r being expressed per unit reactor volume. The operating conditions for the reactor are: $C_{A0}=13$ mol/L, $V=10$ L, $v_0=0.2$

L/s.[12] The Mathcad worksheet for this illustration is shown in Table 5. The symbolic solution of the steady-state mass balance for A, viz., $(C_{A0}-C_A)/\tau = r(C_A)$, reveals that the reactor can operate at three steady states. The students observe that the steady-state mass balance is a cubic equation in the unknown, C_A, and therefore has three solutions, not all of which may be real. The verification of solutions of the steady-state mass balance, generated as a vector, follows as usual and is done at once for all three solutions. The start-up conditions are important in determining which steady state is eventually reached. This requires solution of the mass balance for the transient operation, viz.,

$$\frac{dC_A}{dt} = \frac{(C_{A0}-C_A)}{\tau} - r(C_A), \quad C_A(0) = C_{Ai} \qquad (9)$$

The results of computations pertaining to two C_{Ai} are shown

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TABLE 4
Worksheet for Illustration 4

$P_0 := 1.2 \qquad K_{P1} := 0.45 \qquad K_{P2} := 28.5 \qquad y_{A0} := 0.45$

$y_{B0} := 0.25 \qquad y_{I0} := 1 - y_{A0} - y_{B0} \qquad y_{I0} = 0.3$

$\rho_1 := 0.085 \qquad \rho_2 := 0.132$

Given

$$\frac{\rho_1 \cdot (0.5 \cdot \rho_1 + 1.5 \cdot \rho_2)^{0.5} \cdot P_0^{0.5}}{(y_{A0} - \rho_1 - 2 \cdot \rho_2)} - 0.45 = 0$$

$$\frac{(0.5 \cdot \rho_1 + 1.5 \cdot \rho_2)^{1.5} \cdot (2 \cdot \rho_2)^2 \cdot P_0^{0.5}}{(y_{A0} - \rho_1 - 2 \cdot \rho_2)^2 \cdot (y_{B0} - \rho_2)} - 28.5 = 0$$

$$\begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix} := \text{Find}(\rho_1, \rho_2) \qquad \rho_1 = 0.06 \qquad \rho_2 = 0.157$$

Verify

$$\frac{\rho_1 \cdot (0.5 \cdot \rho_1 + 1.5 \cdot \rho_2)^{0.5} \cdot P_0^{0.5}}{(y_{A0} - \rho_1 - 2 \cdot \rho_2)} - 0.45 = 1.805 \times 10^{-10}$$

$$\frac{(0.5 \cdot \rho_1 + 1.5 \cdot \rho_2)^{1.5} \cdot (2 \cdot \rho_2)^2 \cdot P_0^{0.5}}{(y_{A0} - \rho_1 - 2 \cdot \rho_2)^2 \cdot (y_{B0} - \rho_2)} - 28.5 = -4.707 \times 10^{-7}$$

Equilibrium Composition

$$y_A := \frac{(y_{A0} - \rho_1 - 2 \cdot \rho_2)}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)} \qquad y_B := \frac{(y_{B0} - \rho_2)}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)} \qquad y_C := \frac{\rho_1}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)}$$

$$y_D := \frac{(0.5 \cdot \rho_1 + 1.5 \cdot \rho_2)}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)} \qquad y_E := \frac{2 \cdot \rho_2}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)} \qquad y_I := \frac{y_{I0}}{(1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2)}$$

$y_A = 0.068 \qquad y_B = 0.083 \qquad y_C = 0.054 \qquad y_D = 0.24 \qquad y_E = 0.284 \qquad y_I = 0.271$

$y_A + y_B + y_C + y_D + y_E + y_I = 1 \qquad \psi := 1 + 0.5 \cdot \rho_1 + 0.5 \cdot \rho_2 \qquad \psi = 1.109$

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in Table 5. In this illustration and Illustration 6, integration of appropriate differential equations has been accomplished using the Runge-Kutta method with adaptive step size (Rkadapt). Let the steady state concentrations of A be denoted as C_{As1}, C_{As2}, and C_{As3}, with $C_{As1} < C_{As2} < C_{As3}$. The reactor operation started from C_{Ai1} (very close to but less than C_{As2}) leads to the lowest concentration steady state ($C_{Af1} \rightarrow C_{As1}$, Table 5), while that started from C_{Ai2} (very close to but greater than C_{As2}) leads to the highest concentration steady state ($C_{Af2} \rightarrow C_{As3}$, Table 5). The steady state corresponding to C_{As2} is therefore unstable. Working with other values of C_{Ai}, the students deduce that for $0 < C_{Ai} < C_{As2}$, C_A converges to C_{As1} at large times and for $C_{Ai} > C_{As2}$, C_A converges to C_{As3} at large times (additional computations not shown).

Illustration 6

This illustration pertains to a membrane reactor employed to obtain higher conversions for reversible reactions, and is adapted from Example 4-10 of Fogler.[10] A gas phase dissociation reaction $A \Leftrightarrow B + C$ is carried out in a steady-state plug flow reactor, the wall of which consists of a membrane which allows transport exclusively of B. The feed to the membrane reactor contains only A, with $F_{A0} = 10$ mol/min. The reactor

and the feed are kept at 8.2 atm and 500 K. Since A and C remain in the reaction phase throughout the reactor, it follows from the reaction stoichiometry that $F_C = F_{A0} - F_A$. As there are two independent unit operations (reaction and membrane separation), the two independent mass balances are those for A and B, viz.,

$$\frac{dF_A}{dV} = -r, \quad \frac{dF_B}{dV} = r - r_B \tag{10}$$

The expressions for the volume-specific rates of reaction, r, and removal of B, r_B, are[10]

$$r = k\left(C_A - \frac{C_B C_C}{K_C}\right) = k_1\left[\frac{F_A}{F_T} - C_1 \frac{(F_{A0} - F_A)F_B}{F_T^2}\right],$$

$$r_B = k_B C_B = k_{B1}\frac{F_B}{F_T}, \quad F_T = (F_{A0} + F_B),$$

$$k_1 = kC_{T0}, \quad C_1 = \frac{C_{T0}}{K_C}, \quad k_{B1} = k_B C_{T0}, \quad C_{T0} = \frac{P}{RT} \tag{11}$$

with $k = 0.7$ min^{-1}, $K_C = 0.05$ mol/L, and $k_B = 1$ min^{-1}. It is desired to obtain profiles of F_A and F_B in a 300 L reactor via numerical integration of Eq. (10). The Mathcad worksheet

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TABLE 5
Worksheet for Illustration 5

$$v_0 := 0.2 \qquad C_{A0} := 13 \qquad V := 10 \qquad \tau := \frac{V}{v_0}$$

$$r(C_A) := \frac{C_A}{(1+C_A)^2} \qquad f(C_A) := \frac{(C_{A0} - C_A)}{\tau} - r(C_A)$$

$$C_{As} := f(C_A) \text{ solve, } C_A \rightarrow \begin{pmatrix} .75153576775218804425 \\ 2.1309325629587234809 \\ 8.1175316692890884749 \end{pmatrix} \qquad \overrightarrow{f(C_{As})} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Unsteady state CSTR—Which steady state do we reach? — $C_1 = C_A$

$$t_i := 0.0 \qquad t_f := 10000.0 \qquad Npts := 200 \qquad C_{Ai1} := 2.1305$$

$$D(t,C) := \frac{(C_{A0} - C_1)}{\tau} - \frac{C_1}{(1+C_1)^2} \qquad Sol := Rkadapt(C_{Ai1}, t_i, t_f, Npts, D)$$

$$C_{Af1} := Sol_{Npts,2} \qquad C_{Af1} = 0.752 \qquad C_{Ai2} := 2.1315$$

$$Sol := Rkadapt(C_{Ai2}, t_i, t_f, Npts, D) \qquad C_{Af2} := Sol_{Npts,2} \qquad C_{Af2} = 8.118$$

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for this illustration is shown in Table 6. The students observe that the profile of F_B exhibits a maximum (Table 6), since B is not supplied in the feed and is subject to two serial processes, namely generation by reaction and removal by membrane. If B is not removed by membrane separation (reaction-only operation, $F_B = F_C = F_{A0} - F_A$ per reaction stoichiometry), working with the driving force for the reaction, the lowest F_A ($= F_{Ae}$, corresponding to reaction equilibrium) is calculated via symbolic manipulations to be 5.528 mol/L (Table 6), which corresponds to 45% conversion of A. From the profile of F_A in Table 6, the students observe that for the effluent from the membrane-wall reactor, F_A is much lower than F_{Ae} and therefore the conversion of A is much higher. The last two illustrations deal with multiple reactions.

Illustration 7

This illustration, adopted from Example 6-7 of Fogler,[10] pertains to the series-parallel reactions

$$M + H \rightarrow X + M_e, \quad r_1 = k_1 \sqrt{C_H} C_M$$

$$X + H \rightarrow T + Me, \quad r_2 = k_2 \sqrt{C_H} C_X \qquad (12)$$
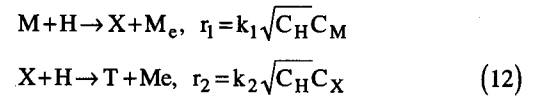
with M, H, X, Me, and T being abbreviations for mesitylene, hydrogen, m-xylene, methane, and toluene, respectively. The reactions are carried out in a CSTR. The feed contains only M and H. In view of the stoichiometry of these mole-conserving reactions, it can be deduced that the concentrations of species influencing the kinetics are related to one

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TABLE 6
Worksheet for Illustration 6

$$P := 8.2 \quad R := 0.082 \quad T := 500 \quad C_{To} := \frac{P}{R \cdot T} \quad C_{To} = 0.2$$

$$k := 0.7 \quad K_C := 0.05 \quad k_B := 1.0 \quad F_{A0} := 10 \quad F_{B0} := 0$$

$$k_1 := k \cdot C_{To} \quad k_{B1} := k_B \cdot C_{To} \quad C_1 := \frac{C_{To}}{K_C} \quad IC := \begin{pmatrix} F_{A0} \\ F_{B0} \end{pmatrix}$$

$$Npts := 100 \quad V_i := 0.0 \quad V_f := 300.0 \quad F_1 = F_A \ \& \ F_2 = F_B$$

$$D(V,F) := \begin{bmatrix} -k_1 \cdot \left[\dfrac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \dfrac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right] \\[6mm] k_1 \cdot \left[\dfrac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \dfrac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right] - k_{B1} \cdot \dfrac{F_2}{(F_{A0} + F_2)} \end{bmatrix}$$

$$Sol := Rkadapt(IC, V_i, V_f, Npts, D) \quad V := Sol^{(1)} \quad F_A := Sol^{(2)} \quad F_B := Sol^{(3)}$$
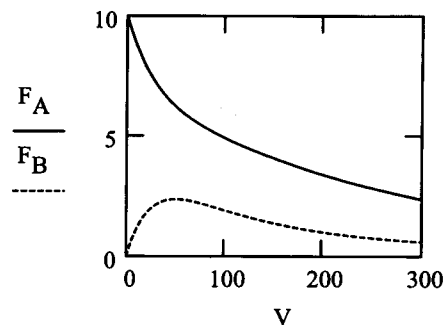
Equilibrium for reaction − only operation

$$G(F_1) := \left[\frac{F_1}{F_{A0} + F_2} - C_1 \cdot F_2 \cdot \frac{(F_{A0} - F_1)}{(F_{A0} + F_2)^2} \right]$$

$$G(F_1) \ substitute, F_2 = F_{A0} - F_1 \rightarrow \frac{F_1}{(20 - F_1)} - 4.0000000000000000000 \cdot \frac{(10 - F_1)^2}{(20 - F_1)^2}$$

$$\left[\frac{F_1}{(20 - F_1)} - 4 \cdot \frac{(10 - F_1)^2}{(20 - F_1)^2} \right] solve, F_1 \rightarrow \begin{pmatrix} 10 + 2 \cdot \sqrt{5} \\ 10 - 2 \cdot \sqrt{5} \end{pmatrix} \quad F_{Ae} := 10 - 2 \cdot \sqrt{5} \quad F_{Ae} = 5.528$$

another as

$$C_M = \tfrac{1}{2}(a + C_H - C_X), \quad a = 2C_{M0} + C_{X0} - C_{H0} \qquad (13)$$

Since there are two independent reactions, one needs to solve only two mass balances, e.g., those for hydrogen and m-xylene, in conjunction with the stoichiometric relation in Eq. (13). The Mathcad worksheet for solution of the design equations is shown in Table 7. The kinetic and operating parameter values are[10]: k_1 = 55.2 (ft³/lb mol)$^{0.5}$/h, k_2 = 30.2 (ft³/lb mol)$^{0.5}$/h, C_{H0} = 0.021 lb mol/ft³, and C_{M0} = 0.0105 lb mol/ft³. The profiles of C_H and C_X are shown in Table 7, with the space time for CSTR—τ_c—being in hours. The profiles reveal that the concentration of m-xylene, an intermediate, exhibits a maxi-

mum as expected, since it is not supplied in the feed.

For each τ_c, one has to provide initial guesses for C_H and C_X, and solve the mass balances iteratively. The same initial guesses may work for certain range of τ_c. This happens to be the case in this illustration. The solutions of mass balances are therefore obtained using τ_c as a floating variable (Table 7). To verify the solution, the normalized residues associated with the mass balances for H and X—reH and reX, respectively—are calculated by substituting C_H and C_X generated by the solution into the mass balances. From the definitions of reH and reX and magnitudes of these displayed in the profiles in Table 7, it is evident that the profiles of C_H and C_X in Table 7 are indeed solutions of the mass balances.

TABLE 7
Worksheet for Illustration 7

$k_1 := 55.2 \qquad k_2 := 30.2 \qquad C_{Ho} := 0.021 \qquad C_{Mo} := 0.0105 \qquad C_{Xo} := 0.0$

$a := 2 \cdot C_{Mo} + C_{Xo} - C_{Ho} \qquad a = 0$

$C_H := 0.0089 \qquad C_X := 0.00312$

Given

$$\frac{(C_H - C_{Ho})}{\tau_c} = -k_1 \cdot (C_H)^{0.5} \cdot (a + C_H - C_X) \cdot 0.5 - k_2 \cdot (C_H)^{0.5} \cdot C_X$$

$$\frac{C_X}{\tau_c} = k_1 \cdot (C_H)^{0.5} \cdot (a + C_H - C_X) \cdot 0.5 - k_2 \cdot (C_H)^{0.5} \cdot C_X$$

$$\mathrm{Sol1}(\tau_c) := \mathrm{Find}(C_H, C_X) \qquad C_H(\tau_c) := \mathrm{Sol1}(\tau_c)_1 \qquad C_X(\tau_c) := \mathrm{Sol1}(\tau_c)_2$$

$$\mathrm{reH}(\tau) := \frac{\tau \cdot \left[-k_1 \cdot (C_H(\tau))^{0.5} \cdot (a + C_H(\tau) - C_X(\tau)) \cdot 0.5 - k_2 \cdot (C_H(\tau))^{0.5} \cdot C_X(\tau) \right]}{C_H(\tau) - C_{Ho}} - 1$$

$$\mathrm{reX}(\tau) := \frac{\tau \cdot \left[k_1 \cdot (C_H(\tau))^{0.5} \cdot (a + C_H(\tau) - C_X(\tau)) \cdot 0.5 - k_2 \cdot (C_H(\tau))^{0.5} \cdot C_X(\tau) \right]}{C_X(\tau)} - 1$$
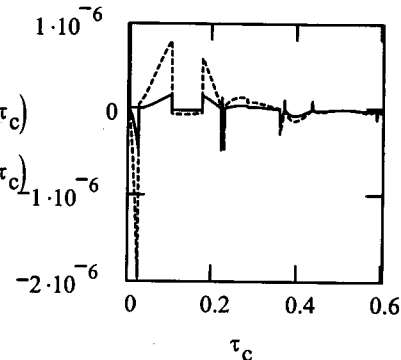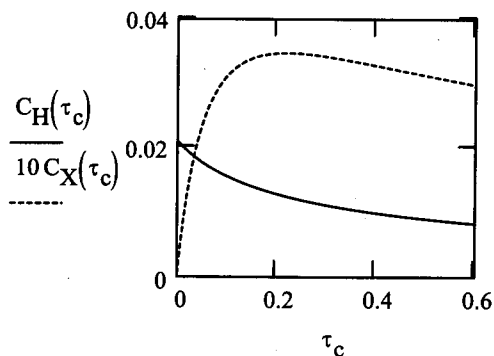
Illustration 8

This illustration, adopted from Example 8-12 of Fogler,[10] pertains to elementary liquid phase reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ taking place in an adiabatic steady state CSTR. The expressions for C_A and C_B obtained from solution of mass balances for A and B are

$$C_A = \frac{C_{A0}}{(1+\tau k_1)}, \quad C_B = \frac{\tau k_1 C_A}{(1+\tau k_2)} \tag{14}$$

The energy balance has the form (specific heats of all species being considered equal, $C_{pA} = C_{pB} = C_{pC} = C_p$)

$$C_{A0}C_P(T-T_0) + (k_1 C_A \Delta H_1 + k_2 C_B \Delta H_2)\tau = 0,$$

$$k_i = k_{i0}\exp\left(-\frac{E_i}{RT}\right), \quad i = 1, 2 \tag{15}$$

Upon substituting Eq. (14) into the above, the master equation for the adiabatic reactor is obtained as

$$G(T) = R_m(T), \quad R_m(T) = C_p(T - T_0),$$

$$G(T) = -\frac{\tau k_1(T)}{[1+\tau k_1(T)]}\left[\Delta H_1 + \Delta H_2 \frac{\tau k_2(T)}{(1+\tau k_2(T))}\right] \tag{16}$$

with the reactor temperature T being the only unknown. The values of various parameters are: C_p=300 J/{mol.K}, ΔH_1 = -55,000 J/mol, ΔH_2 = -71,500 J/mol, C_{A0}=0.3 mol/L, T_0=300 K, τ= 0.01 min, E_1 = 9,900 cal/mol, E_2 = 27,000 cal/mol, k_1 = 3.03 min^{-1} at 300 K, k_2=4.58 min^{-1} at 500 K. With the exception of C_p, all other parameter values have been taken from Fogler,[10] where C_p has been considered to be 200 J/{mol.K} and the reactor operation has been considered to be nonadiabatic. The Mathcad worksheet for this illustration is shown in Table 8. By plotting G(T) and R(T) versus T, the students observe that the two profiles intersect at five T's for T > T_0, implying existence of five steady states. The temperature at each steady state can be calculated via iterative solution of Eq. (16). Alternately, the relative error associated with Eq. (16), denoted as dif(T) in Table 8, can be calculated at various temperatures to directly zoom in on the steady state temperature. For the parameters under consideration, the steady state T values are 309.59, 354.33, 473.85, 540.29, and 719.58 K.

TABLE 8
Worksheet for Illustration 8

$C_P := 300 \quad \Delta H_1 := -55000 \quad \Delta H_2 := -71500 \quad C_{A0} := 0.3 \quad T_0 := 300 \quad \tau := 0.01$
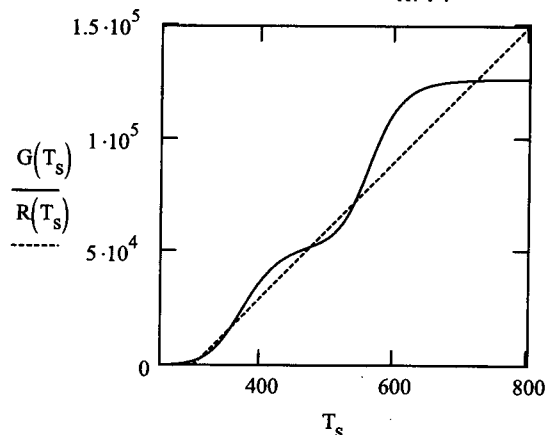
$E_1 := 9900 \quad E_2 := 27000$

$$k_{10} := 3.3 \cdot \exp\left(\frac{E_1}{1.987} \cdot \frac{1}{300}\right) \qquad k_{20} := 4.58 \cdot \exp\left(\frac{E_2}{1.987} \cdot \frac{1}{500}\right)$$

$$k_1(T) := k_{10} \cdot \exp\left(\frac{-E_1}{1.987 \cdot T}\right) \qquad k_2(T) := k_{20} \cdot \exp\left(\frac{-E_2}{1.987 \cdot T}\right)$$

$$G(T) := \frac{-\tau \cdot k_1(T)}{(1+\tau \cdot k_1(T))} \cdot \left[\Delta H_1 + \Delta H_2 \cdot \frac{\tau \cdot k_2(T)}{(1+\tau \cdot k_2(T))}\right]$$

$$R(T) := C_p \cdot (T - T_0) \qquad \text{dif}(T) := \frac{G(T)}{R(T)} - 1.0$$

$\text{dif}(309.59) = 6.249 \times 10^{-5}$

$\text{dif}(354.33) = 2.788 \times 10^{-5}$

$\text{dif}(473.85) = -4.697 \times 10^{-6}$

$\text{dif}(540.29) = -5.812 \times 10^{-6}$

$\text{dif}(719.58) = -1.027 \times 10^{-6}$

DISCUSSION

The students also use Matlab in parallel to Mathcad. Both packages are available on computers across the IIT campus and in the chemical engineering computer laboratory. The purpose of exposing students to different packages is to provide them with a broad spectrum of skills needed for solving engineering problems and to demonstrate the differences in the packages' capabilities for solving different engineering problems.[1] The students recognize that some of the problems can be formulated, but not solved, by hand. They can quickly develop worksheets for these problems and solve them, the emphasis thus being on understanding the fundamentals of the problems.

Care must be taken to ensure that use of computational software enhances students' understanding and enriches their logic and problem-solving skills, rather than simply allowing them to solve problems with only a superficial understanding of the problems.[13] With this in mind, the undergraduate chemical reaction engineering course using this software at IIT includes handouts and tutorials providing an introduction to the software and to different numerical methods. Further, the author has integrated computational software throughout the course, with the use of software always following solution of related simpler problems by hand.[13]

CONCLUSION

The use of computational packages enhances teaching and learning, allowing the teacher to cover more material.[2, 14] In the process, the students learn more and faster and appreciate the course even more, while developing the skills and flexibility necessary for ready adoption of different software packages for professional activities in industry.[1, 4, 10, 14] The graphics capabilities of Mathcad help in quick visualization of results as well as in reinforcing expected results *and* under-

standing not-so-expected results. The capabilities of Mathcad in symbolic manipulations are of considerable use in developing analytical skills of students in solving complex problems. The time spent outside the courses on gaining further familiarity with different computational software and their applications will allow students to reap the benefits of these programs.[14]

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