WHAT TO DO IF RELATIVE VOLATILITIES CANNOT BE ASSUMED TO BE CONSTANT

Differential-Algebraic Equations Systems in Undergraduate Education

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Design and simulation of unit operations and many other physical phenomena require development of mathematical models and a solution of the models. In the past, the analytical solution was the only option. Nowadays, however, with the introduction of interactive, user-friendly numerical software packages, the model is often solved numerically even if an analytical solution can be obtained, since a numerical solution usually requires less effort and allows solution of more realistic problems. Obviously, an analytical expression can provide more information than a numerical solution. While a numerical solution provides numerical information only inside the region where simulation is carried out, an analytical expression allows investigation of the model behavior over the entire region of its validity. Furthermore, when the analytical model is presented in a dimensionless form, the effects of its various (dimensionless) parameters can often be predicted even without solving the equations.

But arriving at an analytical solution often requires simplification of the rigorous model by making certain assumptions. Once an assumption is made, it is sometimes difficult to appreciate the inaccuracy it introduces and to decide whether the solution reached for the simplified model is also a valid solution for the original problem. The information provided by analytical and numerical solutions complement each other, and therefore it is very important to obtain both whenever it is possible. The recommended procedure would start with solving the simplified model both analytically and numerically. This apparently superfluous step validates the analytical solution of the simplified model and at the same time substantiates the numerical scheme. Then one can proceed to solve the rigorous model numerically.

If the rigorous model consists of ordinary differential equations (ODE) or nonlinear algebraic equations (NLE), the numerical solution is a feasible approach, even at an undergraduate level, using readily available software tools such as MAPLE,[1] MATLAB,[2] and POLYMATH.[3] Often, rigorous models of simple systems contain both ordinary differential equations and implicit nonlinear algebraic equations. Such a system of equations is called a differential-algebraic system (DAE). The software tools available for solving such

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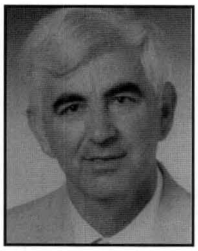

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In this paper, we present two simple examples where some simplified models yield incorrect results and there is a need to solve DAE systems. A simple technique for solving DAE systems using the software tools familiar to engineering students is introduced.

systems are not yet appropriate for use by undergraduate students, and instructors feel reluctant to present realistic models containing DAEs.

In this paper, we present two simple examples where some simplified models yield incorrect results and there is a need to solve DAE systems. A simple technique for solving DAE systems using the software tools familiar to engineering students is introduced.

FORMULATING SIMPLIFIED AND RIGOROUS MODELS FOR BINARY BATCH DISTILLATION

Calculation of the composition in a batch distillation still as a function of the amount of the remaining liquid is a classical problem, described in many textbooks.[4-7] The simplified model for batch distillation was provided by Lord Rayleigh in 1902.[8]

The batch distillation apparatus is shown schematically in Figure 1. Liquid of the amount L_o moles is initially charged into the still. Distillate is removed continuously at a rate of V moles/hr. Total material and component balances on the still yield

$$\frac{dL}{dt} = -V \qquad L(t=0) = L_o \tag{1}$$

$$\frac{d(Lx_i)}{dt} = -V y_i \tag{2}$$

where x_i is the mole fraction of species i in the liquid phase, and y_i is the mole fraction of species i in the vapor phase. Equations (1) and (2) are combined to yield

$$\frac{dL}{dx_i} = \frac{L}{y_i - x_i} \qquad x_i(t=0) = x_{io} \tag{3}$$

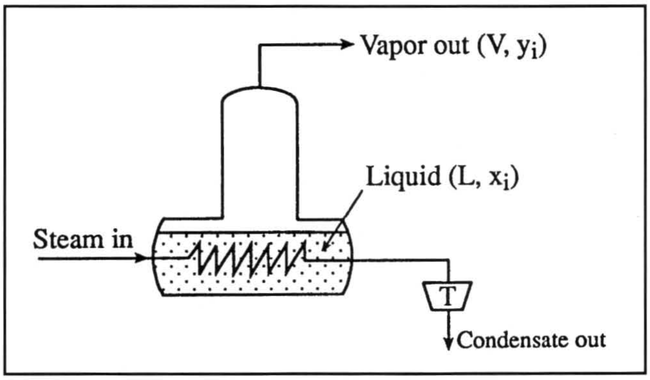

Figure 1. *Batch distillation apparatus.*

The solution of Eq. (3) requires an equilibrium relationship between y_i and x_i. Such a relationship can be expressed using either the vapor liquid equilibrium ratio k_i or the relative volatility α_{ij}. During distillation, the liquid and vapor compositions change. Consequently, the temperature changes, following the bubble point curve of the liquid. If the value of k_i can be assumed to be constant, Eq. (3) can be integrated from the initial mole fraction of species i, x_{io} to the final mole fraction x_i, to yield

$$\ell n\left(\frac{L}{L_o}\right) = \frac{1}{k_i - 1}\ell n\left(\frac{x_i}{x_{io}}\right) \tag{4}$$

For a binary system when α_{ij} is assumed to be constant, integration of Eq. (3) yields

$$\ell n\left(\frac{L}{L_o}\right) = \frac{1}{\alpha_{ij} - 1}\ell n\left[\frac{x_i(1-x_{io})}{x_{io}(1-x_i)}\right] + \ell n\left(\frac{1-x_{io}}{1-x_i}\right) \tag{5}$$

To verify that either k_i or α_{ij} may be assumed to be constant, the bubble point temperature at the initial and final compositions and the respective k_i and α_{ij} values must be calculated. If there is only a small difference between the initial and final values, an average value of k_i or α_{ij} can be used in Eqs. (4) or (5), respectively. But when a considerable difference is encountered, the simplified model gives incorrect results and the rigorous model must be used.

In the rigorous model, the effect of changing compositions and temperature during the distillation on the k_i and α_{ij} values must be taken into account. The temperature changes in the batch still follow the bubble point curve. The bubble point temperature is defined by the implicit algebraic equation

$$f(T) = 1 - \sum_i k_i x_i = 0 \tag{6}$$

For near-atmospheric pressures, the vapor-liquid equilibrium ratio can be expressed by

$$k_i = \frac{\gamma_i P_i}{P} \tag{7}$$

where P_i, γ_i are the vapor pressure and the activity coefficients of the species, respectively, and P is the total pressure (usually constant).

The vapor pressure of an individual component can be correlated as a function of temperature using, for example, the Antoine equation. The activity coefficient for a binary system can be expressed as a function of the liquid composition using Margules, Van-Laar, or similar equations.

The system of equations comprising Eqs. (3), (6), and (7) is a DAE system. Thus, if neither k_i nor α_{ij} can be assumed to be constant, the solution of a binary batch distillation problem requires a numerical solution of a DAE system.

NUMERICAL SOLUTION OF THE SIMPLIFIED AND RIGOROUS MODELS

The results of the simplified model and the rigorous model are compared by solving both numerically. The initial temperature and the associated k_i and α_{ij} values are obtained by solving the bubble point temperature, Eq. (6), at the initial composition. From this initial point, the ODE equation, Eq. (3), can be integrated while maintaining constant (say, the initial) values for the temperature, k_i and α_{ij}. The error introduced by this assumption is estimated from Eq. (6), which is rewritten in the form

$$\varepsilon = 1 - \sum_i k_i x_i \tag{6a}$$

The error calculated from Eq. (6a) provides a basis for correcting the temperature along the bubble point curve. The temperature can be changed in proportion to the error. Thus

$$\frac{dT}{dx_i} = K_c \varepsilon \tag{8}$$

A proper choice of K_c will keep the error below a desired error tolerance ε_d throughout the whole integration interval. Equations (6a) and (8) combined yield an ODE system that represents the rigorous model.

This method for solving a DAE system by converting it to an ODE system will be called the "controlled integration" method. The name indicates that the variation of the algebraic variable is being controlled during the integration to maintain the error of the implicit algebraic equation below a desired level.

The value of K_c, appropriate for a certain error tolerance, can be estimated from the rate of increase of the error while the temperature is kept constant. A method for calculating K_c is explained in Appendix A. The value of K_c can also be determined by a simple trial-and-error technique. Students often find this approach easier to understand and more convenient to implement. It will be demonstrated in the detailed example that follows.

Another option to convert a DAE system into an ODE system is differentiation of the implicit algebraic equation(s) (such as Eq. 6) to obtain an expression for, say, dT/dx_i. For initialization (to get an initial value for T), the implicit algebraic equation(s) must be solved. This approach has several disadvantages in comparison to the controlled integration method. The differentiation of even moderately complex equations is a very tedious and error-prone task. Furthermore, it is often impossible to express the differential (say, dT/dx_i) explicitly, as is required by most numerical software tools. The use of this method becomes especially complicated for disjunctive system of equations, where there is a need to use different sets of equations in different regions (transition from laminar to turbulent flow, for example). The transition from one region to another requires re-initialization of the system, while for the controlled integration method, such a re-initialization is not necessary. The use of differentiation for converting DAEs to ODEs, and the potential difficulties, will also be demonstrated in the examples that follow.

EXAMPLE 1

Batch Distillation of an Ideal and a Non-Ideal Binary System

1a. Ideal System

King[4] presents an example of batch distillation of benzene (component #1) and toluene (component #2) mixture. Initially, there are 100 moles of liquid in the still, comprising 60% benzene and 40% toluene (mole fraction). The amount of liquid remaining in the still when the concentration of toluene reaches 80% should be calculated. The distillation is

TABLE 1
Initial and Final Conditions in Batch Distillation of a Benzene (1) Toluene (2) Mixture

	x_1	x_2	T°C	k_1	k_2	α_{12}
Initial	0.6	0.4	95.5851	1.31164	0.532535	2.46302
Final	0.2	0.8	108.572	1.85674	0.785817	2.36281

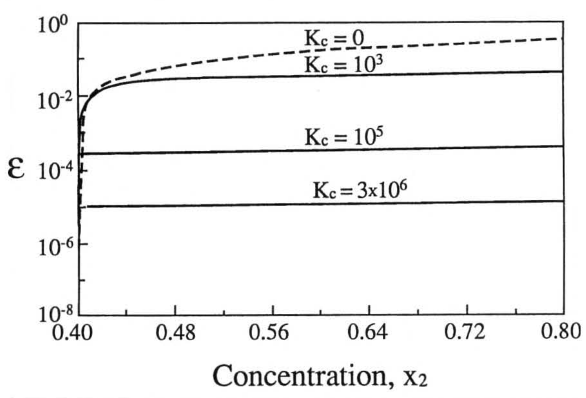

Figure 2. *Variation of ε while changing the value of K_c in Eq. (8).*

carried out at a pressure of 1.2 atm.

The mixture of toluene and benzene can be considered as an ideal mixture ($\gamma_1, \gamma_2 = 1$), thus the liquid vapor equilibrium ratio can be calculated from $k_i = P_i/P$. The vapor pressure of the individual components can be calculated from the Antoine equation

$$\log(P_i) = A_i + \frac{B_i}{T + C_i} \tag{9}$$

where P_i is the pressure in mmHg, and T is the temperature in °C. The Antoine equation constants for benzene are $A_1 = 6.90565$, $B_1 = -1211.033$, and $C_1 = 220.79$. For toluene they are $A_2 = 6.95464$, $B_2 = -1344.8$, and $C_2 = 219.482$.[9]

Solving the algebraic Eq. (6) (when k_i is calculated from Eqs. 7 and 9) to find the bubble point temperature at the initial and final composition of the liquid, yields the results shown in Table 1.

It can be seen that the temperature increases during the distillation by about 13°C, which causes approximately a 40% increase in the value of k_1 but only about a 4% reduction in the value of α_{12}. Thus, Eq. (5), with an average value of $\alpha_{12} = 2.41$, can be used to calculate the amount of liquid remaining in the still. This calculation yields L = 14.031 mol, which is identical to the result obtained by King.[4]

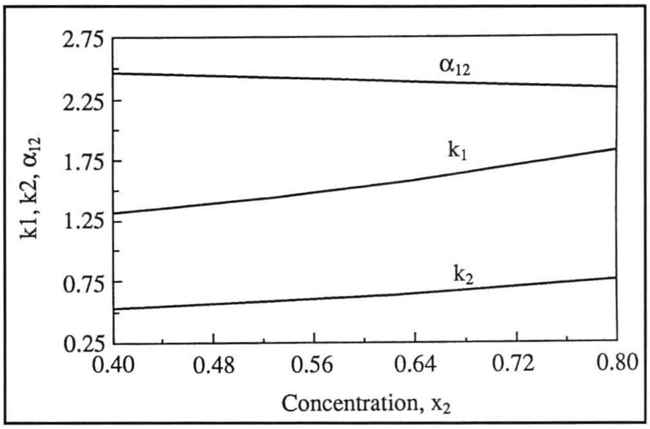

Figure 3. *Variation of k_1, k_2, and α_{12} during distillation of the ideal benzene-toluene system.*

TABLE 2
Antoine Equation Constants[9] for the Water-Ethanol System

	A	B	C
Water	7.96681	-1668.21	228.0
Ethanol	8.04499	-1554.3	222.65

TABLE 3
Initial and Final Conditions in Batch Distillation of a Water (1) and Ethanol (2) Mixture

	x_1	x_2	T°C	k_1	k_2	α_{12}
Initial	0.4	0.6	79.1685	0.757729	1.16151	0.652364
Final	0.95	0.05	90.9639	0.721619	6.28615	0.114795

To check whether the results of the simplified model are accurate enough, numerical integration of Eq. (3) is carried out while the error is calculated using Eq. (6a). Since numerical integration must proceed in the direction of increasing x_2 value, Eq. (3) is integrated from $x_2 = 0.4$ up to $x_2 = 0.8$. Figure 2 shows that various values of K_c yield solutions of different precision. For $K_c = 0$, ε increases from -3.6×10^{-7} at the initial point to 0.311 at the final point. With $K_c = 1000$, the maximal error is 3.7×10^{-2} and it reduces to 3.9×10^{-4} for $K_c = 10^5$.

Finally, using $K_c = 3 \times 10^6$ yields a solution with a maximal error $\varepsilon = 1.3 \times 10^{-5}$ at $x_2 = 0.8$, which matches the desired error tolerance ($\varepsilon_d = 10^{-5}$). The initial and final values for the other variables are exactly the same as shown in Table 1. The remaining liquid, L = 14.0423 mol, differs only in the fourth decimal digit from the simplified model results. The reason for the excellent fit in this case is that the relative volatility changes linearly over the entire range (see Figure 3). Thus, an average value of α_{12} provides a very good representation.

In this example, the rigorous model is simple enough to obtain an analytical expression for dT/dx_2. For an ideal binary mixture, where $\gamma_i = 1$ and the vapor pressure is represented by the Antoine equation, differentiation of Eq. (6) yields

$$\frac{dT}{dx_2} = \frac{(k_2 - k_1)}{\ell n(10)\left(x_1 k_1 \frac{B_1}{(C_1 + T)^2} + x_2 k_2 \frac{B_2}{(C_2 + T)^2}\right)} \tag{10}$$

Simultaneous numerical integration of Eqs. (3) and (10) yields the same results as were obtained using the controlled integration method.

1b. Non-Ideal System

The batch distillation of the ideal-system example is repeated with the non-ideal mixture of water (component #1) and ethanol (component #2). Initially, a liquid mixture of 60% ethanol and 40% water is charged to a still pot. The distillation is carried out at a total pressure of 1 atm. The amount of liquid remaining in the still, when the mole fraction of water reaches 0.95, should be calculated.

Since water and ethanol form a non-ideal mixture, Eq. (7) should be used to calculate the vapor-liquid equilibrium ratio. The Margules equations can be used to calculate the activity coefficients of the various components:

$$\log(\gamma_1) = x_2^2\left[a + 2x_1(b-a)\right] \tag{11a}$$

$$\log(\gamma_2) = x_1^2\left[b + 2x_2(a-b)\right] \tag{11b}$$

where a=0.3781 and b = 0.6848 for this particular system.[10] The respective Antoine equation constants are shown in Table 2.

Solving the algebraic equations for bubble point temperature at the initial and final compositions of the liquid yields the results shown in Table 3.

It can be seen that in this case changes in the values of the relative volatility and k_2 are very significant. Using Eq. (5) with an average value of α_{12}=0.384 to calculate the remaining amount of liquid yields L = 5.236 moles.

The rigorous model is solved by the controlled integration method. Using the procedure described in Appendix A with an error tolerance of $\varepsilon_d = 10^{-5}$ yields $K_c = 2.56 \times 10^5$. The amount of liquid remaining in the still using the rigorous model is L = 8.329 moles, 60% greater than the value predicted by the simplified model. Figure 4 shows the variation of k_1, k_2, and α_{12} during distillation. It can be seen that the variation of α_{12} is nonlinear. This explains the large discrepancy between the results of the simplified and rigorous models.

For this non-ideal solution, Eq. (6) can be differentiated to yield

$$\frac{dT}{dx_1} = \frac{(k_1 - k_2) + \left(\frac{\partial\gamma_1}{\partial x_1} - \frac{\partial\gamma_1}{\partial x_2}\right)x_1\frac{P_1}{P} + \left(\frac{\partial\gamma_2}{\partial x_1} - \frac{\partial\gamma_2}{\partial x_2}\right)x_2\frac{P_2}{P}}{x_1\frac{\gamma_1}{P}\frac{dP_1}{dT} + x_2\frac{\gamma_2}{P}\frac{dP_2}{dT}} \tag{12}$$

To carry out all the differentiations required in Eq. (12) can probably be a good exercise in mathematics, but it is clearly not a practical way to solve the rigorous model. Even when a symbolic manipulation package (such as Maple) is used to carry out the differentiations, the effort and the complexity involved are not reduced to such a level that makes this approach a practical one to be used in undergraduate education.

EXAMPLE 2

Draining a Cylindrical Tank

Figure 5 shows a cylindrical tank of diameter D with a draining pipe arrangement. The initial height of the liquid level above the draining pipe exit is H_0 and the final height is H_f. The draining pipe diameter is d and its length is L. The time required to drain the tank from the initial height of H_0 to the final height H_f is to be calculated.

The equations representing the tank during the draining are fairly simple and have been discussed widely in the literature.[11,12] The pertinent equations follow.

The rate of change of the liquid level in the tank dH/dt is

$$\frac{dH}{dt} = -\frac{d^2}{D^2}V_2 \tag{13}$$

where V_2 is the exit velocity of the liquid from the draining pipe,

$$V_2 = \sqrt{\frac{2g(H+L)}{1 + f_D L/d}} \tag{14}$$

In the laminar region (Re ≤ 2100), the friction factor, f_D, is given by

$$f_D = \frac{64}{Re} \tag{15}$$

where Re is the Reynold's number, Re = $V_2 d/\upsilon$, and υ is the kinematic viscosity. In the turbulent region (Re ≥ 4000),, the Colebrook & White equation applies:

$$\frac{1}{\sqrt{f_D}} = -2\log\left(\frac{e}{3.7\,d} - \frac{2.51}{Re\sqrt{f_D}}\right) \tag{16}$$

where e is the pipe roughness.

Assuming that f_D is constant during draining, the expres-

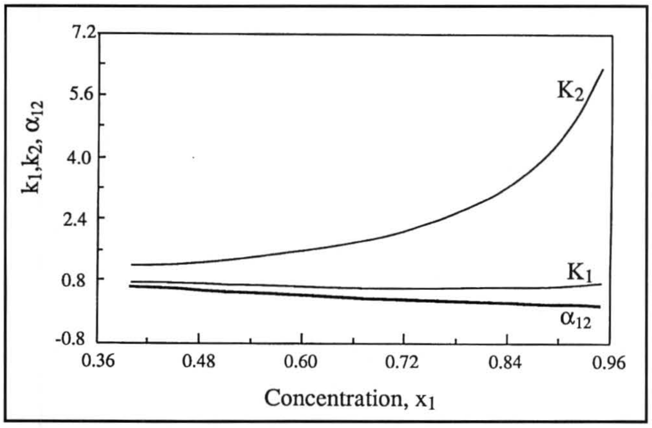

Figure 4. *Variation of k_1, k_2, and α_{12} during distillation for the non-ideal water-ethanol system.*

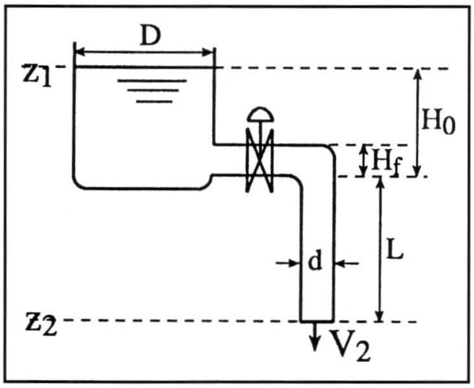

Figure 5. *Tank with draining pipe.*

sion for V_2 from Eq. (14) can be introduced into Eq. (13). Integration from H_0 to H_f yields the expression for the total time required for draining, t_f,

$$t_f = \frac{D^2}{d^2}\sqrt{\frac{2}{g}\left(1+\frac{f_d L}{d}\right)}\left(\sqrt{H_0+L}-\sqrt{H_f+L}\right) \tag{17}$$

The solution of the simplified model (Eq. 17) is compared with the rigorous solution for the case of turbulent draining (Example 2a) and for the case where transition from turbulent to laminar flow takes place during the draining.

2a. Tank Draining in the Turbulent Region

The following numerical data was used for the calculations in the turbulent region: $D = 3$ ft, $H_0 = 3$ ft, and $H_f = 1$ in. The draining pipe is a nominal 1/2" schedule 40 steel pipe with roughness $e = 0.00015$ ft. The liquid in the tank is water at 60°F (kinematic viscosity $\upsilon = 1.22 \times 10^{-5}$ ft^2/s).

The initial and final conditions obtained by solving the system of algebraic equations (comprising Eqs. 14 and 16) are shown in Table 4.

It can be seen that although the exit velocity and the Reynolds number are significantly reduced (to about half of their initial value), the friction factor changes only by about 6%. Using the average value of $f_D = 0.0291$ in Eq. (17) yields a draining time of $t_f = 1000.58$ s.

TABLE 4
Initial and Final Conditions in Turbulent Draining

	Liquid Level (ft)	Exit Velocity (ft/s)	Re	f_D
Initial	3	12.9157	54873.9	0.02821
Final	0.08333	6.64831	28246.2	0.02998

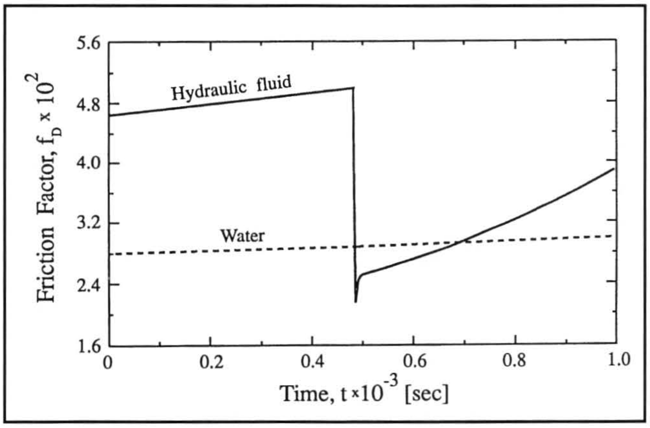

Figure 6. *Friction factor variation during tank draining.*

To solve the rigorous model, Eq. (16) is rewritten as

$$\varepsilon = \left\{-2\log\left(\frac{e}{3.7\,d}-\frac{2.51}{\mathrm{Re}\sqrt{f_D}}\right)\right\}^{-2} - f_D \tag{18}$$

with an additional differential equation

$$\frac{df_D}{dt} = K_c \varepsilon \tag{19}$$

Applying the same procedure used in the batch distillation example for calculating K_c yields the value of $K_c = 1$. Solving the rigorous model by numerical integration yields a draining time of $t_f = 999.5$ s. Thus, the difference between the values calculated by the simplified and rigorous models is insignificant (about 0.1%).

Figure 6 shows the change of the friction factor during draining. The almost linear and very moderate change of f_D causes the simplified model to be very accurate in this example.

2b. Tank Draining in the Transitional and Laminar Regions

The system geometry is the same as in Example 2a, but the liquid in the tank is now hydraulic fluid (MIL-M-5606) at 60°F (kinematic viscosity $\upsilon = 20.9 \times 10^{-5}$ ft^2/s).

The initial and final conditions obtained by solving a system of algebraic equations (comprising Eqs. 14 and 15 or 16) are shown in Table 5. It can be seen that initially the flow is in the transitional region ($2100 < \mathrm{Re} < 4000$). There is no definite rule for the friction factor correlation that applies in this region.[13] The equation for laminar flow (Eq. 15) yields a friction factor smaller by a factor of about 2.5 than the Colebrook & White equation (Eq. 16) for turbulent flow. Consequently, the draining velocity and the Reynolds number are also considerably different.

At the final stage of the draining, the flow is in the laminar region. In order to model this system, we used the Colebrook & White equation for f_D as long as $\mathrm{Re} > 2100$, and Eq. (15) was used after the value of Re dropped for the first time below the value of 2100.

TABLE 5
Initial and Final Conditions During Tank Draining in the Transitional and Laminar Regions

		Liquid Level (ft)	Exit Velocity ft/s	Re	f_D
Initial	f_D from Eq. 15	3	13.7525	3410.77	0.01876
	f_D from Eq. 16	3	11.6509	2889.5	0.04653
Final		0.08333	6.2263	1544.18	0.0414459

Using an average value of $f_D = 0.04399$ in Eq. (17) yields a draining time of t_f - 1088.76 s. Solving the rigorous model using the controlled integration method yields $t_f = 1057.9$ s. Thus, there is only a 3% difference between the results obtained by the simplified and rigorous models. It is to be noted that the difference increases as the period of laminar draining extends.

Figure 6 shows the change of the friction factor during draining. It can be seen that it increases gradually during draining until the Reynolds number reaches Re = 2100 for the first time. At this point, the friction factor calculation switches to the laminar flow equations. This causes the friction factor to drop to about half of the turbulent flow value.

In Figure 7, a similar jump in the exit velocity is noticeable at the point where the flow regime changes. From this point on, the friction factor starts increasing gradually as the flow stays in the laminar regime.

If we attempt to solve this problem by differentiating Eq. (16) to obtain an expression for df_D/dt for converting the original DAE system into an ODE system, the system must be reinitialized at the point of transition from turbulent to laminar flow. The controlled integration method automatically adjusts to such a discontinuity caused by switching between the two different correlations for the friction factor.

ADVANCED TOPICS

The controlled integration method, as presented in the previous sections, enables students without any background in numerical analysis or control theory to solve simple DAE systems using interactive computational tools they are familiar with. For students who have been exposed to process control principles, the method can be extended to include more complex DAE systems using PID controllers.

A DAE system can be written in general as

$$\frac{d\mathbf{x}}{dt} = f(\mathbf{x}, \mathbf{y}, t) \qquad \mathbf{x} = \mathbf{x}^0 \quad \text{at} \quad t = t^0 \tag{20a}$$

and

$$\mathbf{g}(\mathbf{x}, \mathbf{y}, t) = 0 \tag{20b}$$

For solving this system using the controlled integration method, Eq. (20b) is rewritten as

$$\boldsymbol{\epsilon} = \mathbf{g}(\mathbf{x}, \mathbf{y}, t) \tag{20c}$$

and the following equations are added:

$$\frac{d\mathbf{y}}{dt} = \mathbf{q} \tag{20d}$$

$$\mathbf{q} = \mathbf{K}_c \left(\boldsymbol{\epsilon} + \frac{1}{\boldsymbol{\tau}_i} \int_0^t \boldsymbol{\epsilon}\, dt + \boldsymbol{\tau}_D \frac{d\boldsymbol{\epsilon}}{dt} \right) \tag{20e}$$

The set of algebraic equations (Eq. 20b) is solved at the initial point; thus $\mathbf{y} = \mathbf{y}^0$ at $t = t^0$ so that $g(\mathbf{x}^0, \mathbf{y}^0, 0) = 0$. For rigorous solution of the DAE system, controller(s) are used to force **y** to follow the solution curve. The method for selecting the controller type and the tuning parameter values is discussed in detail by Shacham, *et al.*[14]

Students who have access to large-scale dynamic simulation programs (such as SPEEDUP[15]) can solve DAE systems directly, just like ODE systems. Unfortunately, these large-scale packages are still too complex to be used in undergraduate education.

SUMMARY AND CONCLUSIONS

We have shown that application of closure laws in realistic modeling will often lead to the need to solve DAE systems. Educators in the past were reluctant to discuss such problems because there were no software tools available to enable students to solve DAEs.

We have introduced the controlled integration method, which enables students without prior knowledge of numerical analysis or process control, to solve simple DAE systems using user-friendly popular software tools, such as MAPLE, MATLAB, and POLYMATH.

The examples presented clearly demonstrate that without solving the rigorous model, the error introduced by certain simplifying assumptions often cannot be appreciated. There is no justification whatsoever to avoid classroom problems (where, say, the relative volatility is not constant) just because an elegant analytical solution does not exist. Just as user-friendly NLE solvers enable students to deal with real gases represented by various equations of state (in addition to the ideal gas), the method presented in this paper enables them to deal with non-ideal solutions in addition to the traditional treatment of ideal solutions.

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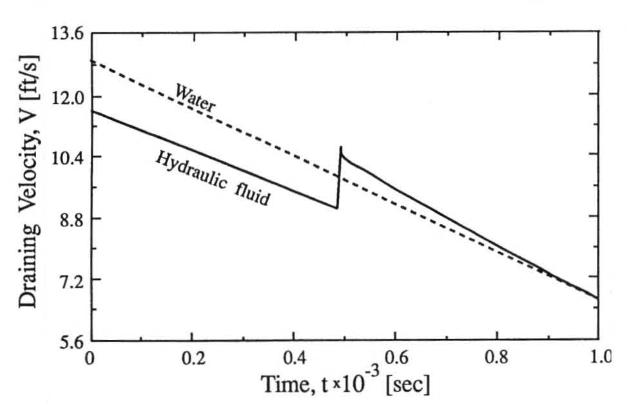

Figure 7. *Velocity variation during draining.*

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APPENDIX A

Calculation of the Controlled Integration K_c for the Batch Distillation Problem

The change of temperature in the batch still can be expressed by the differential equation

$$\frac{dT}{dx_i} = -\frac{\partial T}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial x_i} \qquad (A-1)$$

Both derivatives on the right-hand side of this equation can be easily estimated by integrating the simplified model, observing the change of ε vs. x_i while keeping T constant. The slope of the curve $\Delta\varepsilon / \Delta x$ yields an estimation for $\partial\varepsilon / \partial x_i$. Introducing a small change in the temperature, ΔT, and measuring the resultant change in the error, $\Delta\varepsilon$ provides an estimate for $\partial T / \partial\varepsilon \sim \Delta T / \Delta\varepsilon$. In order to keep the error within a desired error tolerance, $(|\Delta\varepsilon| \le \varepsilon_d)$ the integration step size, Δx_i should be of the order of $\varepsilon_d / (\Delta\varepsilon / \Delta x_i)$.

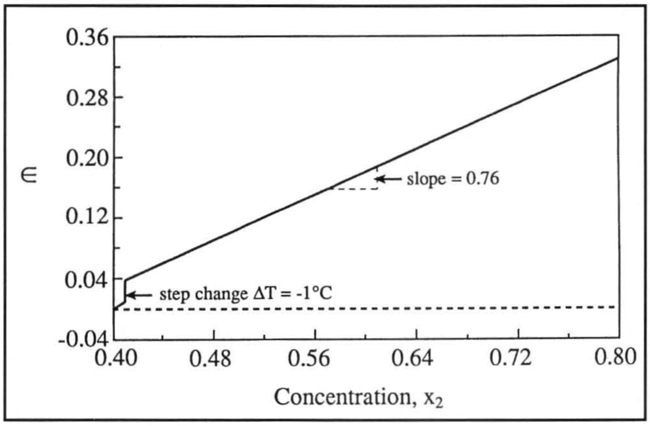

Figure A-1. *Variation of the error in the bubble point equation for the constant temperature batch distillation model.*

Comparing Eq. (8) with Eq. (A-1) shows that

$$K_c \approx -\frac{\partial T}{\partial \varepsilon}\frac{1}{\Delta x_i}$$

Thus, the value of Δx_i and $\Delta T / \Delta\varepsilon$ can be used to obtain an appropriate value for K_c.

It should be emphasized that only a rough estimate for K_c is needed. Most recent integration routines include step size control algorithms, which will change the value of Δx_i to make Eq. (8) an accurate representation of dT/dx_i. The calculation of K_c is demonstrated with reference to Figure A-1, which shows the variation of ε vs. x_2, for the example of batch distillation of the benzene-toluene mixture. The temperature is kept constant during the integration, except a step change of -1°C, which is introduced at $x_2 = 0.41$.

It can be seen that ε increases linearly from an initial value close to 0 to about 0.36 for $x_2 = 0.8$. The slope of the straight line yields $\partial\varepsilon / \partial x_2 \approx 0.76$. Thus, in order to achieve a solution with a tolerance $\varepsilon_d \cong 10^{-5}$, the controlled integration should use a step size

$$\Delta x_2 \approx \frac{10^{-5}}{0.76} = 1.3 \times 10^{-5}$$

The step change introduced in the temperature (-1°C) causes an increase in the error ($\Delta\varepsilon = 0.028$), hence

$$\frac{\partial T}{\partial \varepsilon} \approx \frac{-1}{0.028} = -35.7$$

An appropriate value for K_c is thus $K_c = 35.7/1.3 \times 10^{-5} = 2.7 \times 10^{6}$. ❐