INTRODUCING DAE MODELS IN UNDERGRADUATE AND GRADUATE

Chemical Engineering Curriculum

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Models play an important role in understanding chemical engineering systems. While Ordinary Differential Equation (ODE) models for physical systems are well covered in the undergraduate curriculum, not much attention is paid to DAE models of chemical engineering systems. DAE models arise naturally in several chemical/physical systems that admit quasi steady-state approximations. Common examples of these can be found in separation and reaction systems. While these models can be thought of as a natural extension to ODE models, there are several new concepts that arise when one considers DAE systems. These are the index of the system, consistent initialization, and so on. Some of these concepts might seem abstract for chemical engineering undergraduates. There is a need to teach these ideas at an undergraduate level, however, as these types of models are becoming commonplace.

In this article, we propose a simple reactive flash as an excellent vehicle for introducing DAE systems to chemical engineering undergraduates. The power of this example is that it allows DAE systems to be introduced naturally in several courses. While one obvious place to introduce this example is after a discussion of ODE systems in a mathematical methods course, this example can be equally easily incorporated into a thermodynamics course. A concomitant solution approach that is a straightforward extension of the Rachford-Rice procedure can be taught for solving flash problems. The reactive flash increases the complexity of the flash calculation by one level through the inclusion of reactions to phase equilibrium. The rest of the article is organized as follows: In the section 1, a simple reactive flash model is discussed with all the assumptions involved. The steady state solution of the reactive flash system through a modified Rachford-Rice procedure is then proposed. In section 2, we show how the more involved ideas, such as the index of a DAE and consistent initialization, can be discussed in the context of this chemical engineering problem.

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1. THE REACTIVE FLASH PROBLEM

Reactive Distillation (RD) is an intensification process involving the combined operation of reaction and separation in a single processing unit. For a detailed review of the various chemical systems that can benefit from the concept of RD, refer to Sundmacher and Kienle.[1] In many of these cases, combining reaction and separation can lead to increased conversion, high selectivity, and reduced capital investment. RD is useful when the chemical system involves reversible reactions, azeotropes, and undesired product formations.

The idea of RD can be explained to undergraduates through a simple reactive flash, which is an extension of the equilibrium flash problem. The reactive flash can be thought of as an idealization of a single stage in an RD column. In this process, the two streams exiting from the reactive flash are assumed to be in phase equilibrium and the ratio of the reaction rate to the mass transfer rate is given by a dimensionless number, called the Damköhler number. Additional assumptions of isothermal and isobaric behavior further simplify the problem formulation. A model for the reactive flash is discussed next.

1.1 Reactive Flash Model

The single-stage, isothermal, isobaric, reactive flash being considered is shown in Figure 1. The following assumptions, which simplify the model equations, are made while formulating the process model[2]:

1. Liquid and vapor leaving the stage are assumed to be in equilibrium
2. Liquid hold up is assumed to be constant
3. Isobaric and isothermal process
4. Non-ideality of liquid phases
5. Reaction takes place in the liquid phase

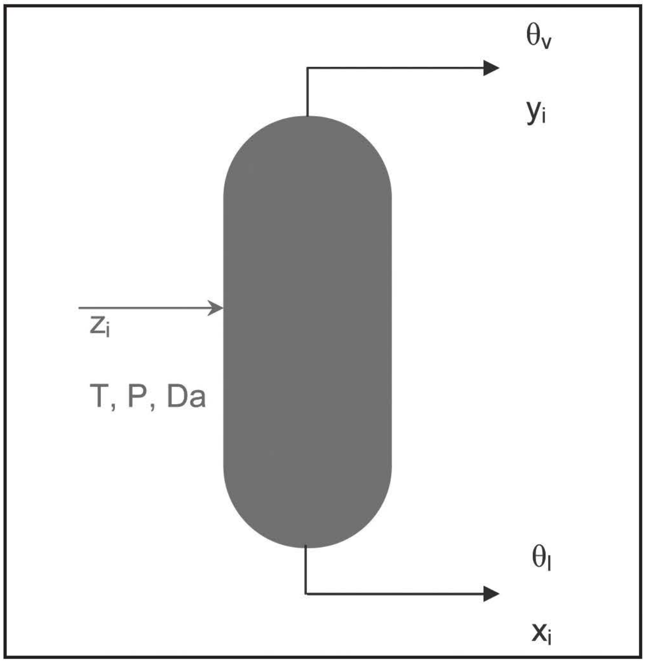

Figure 1. Schematic of a reactive flash.

The equations used to describe this dynamical system are

$$\begin{aligned}
&H\frac{dx_i}{dt} = Fz_i - Lx_i - Vy_i + H\nu_i\varepsilon \\
&y_i = K_i x_i \\
&\text{where } K_i = \frac{\gamma_i P_i^{sat}}{P} \qquad (1) \\
&\sum x_i = 1 \\
&\sum y_i = 1
\end{aligned}$$

L and V are liquid and vapor flow rates; x_i and y_i are liquid and vapor mole fractions respectively; F is the feed flow rate; H is the liquid hold up; the Damköhler number,

$$Da = \frac{H/F}{1/k_{ref}},$$

is a dimensionless ratio of the characteristic liquid residence time to the characteristic reaction time; ν_i is the stoichiometric coefficient; ε is the extent of the reaction; γ_i is the activity coefficient; K_i is the equilibrium constant; and the index i runs from 1 to n, where n is the number of components in the system. k_{ref} is the forward rate constant evaluated at a reference temperature. Introducing the dimensionless variables,

$$\theta_l = \frac{L}{F},\ \theta_\nu = \frac{V}{F}$$

and the dimensionless time, $\tau = t/(H/F)$, the dynamic state equation becomes

$$\begin{aligned}
&\frac{dx_i}{d\tau} = z_i - \theta_l x_i - \theta_\nu y_i + \frac{Da}{k_{ref}}\nu_i\varepsilon \ (2a) \\
&y_i = K_i x_i \ (2b) \qquad (2) \\
&\sum x_i = 1 \ (2c) \\
&\sum y_i = 1 \ (2d)
\end{aligned}$$

A simple degrees-of-freedom analysis will show that there are n differential equations and n+2 algebraic equations making up a total of 2n+2 equations. The number of variables are the n vapor mole fractions, n liquid mole fractions, and the 2 normalized flows, resulting in a total of 2n+2 variables.

1.2 Modified Rachford-Rice for the Steady State Solution of a Reactive Flash Problem

The steady state version of the reactive flash problem can be introduced as a natural extension to the flash problem. The steady state solution to the reactive flash problem can be derived as a modified Rachford-Rice procedure,[3] as discussed below, in cases where the equilibrium constants are either constant or functions of liquid mole fractions.

Defined as

$$R_i = H\nu_i\varepsilon / F \qquad (3)$$

$$\Psi = \sum_i R_i \qquad (4)$$

As we solve the steady state by setting the differential term in equation (2) to zero, we get

$$\left(z_i - \theta_1 x_i - \theta_\nu y_i\right) + R_i = 0 \qquad (5)$$

Since

$$\sum_i \left(y_i - x_i\right) = 0 \qquad (6)$$

and

$$x_i = \frac{z_i + R_i}{\theta_1 + K_i\theta_\nu} \qquad (7)$$

through substitution, we arrive at

$$\sum_i \frac{z_i + R_i}{\left(\theta_1 + \theta_\nu K_i\right)}\left(K_i - 1\right) = 0 \qquad (8)$$

Summation of Eq. (5) over all the components gives

$$\theta_1 = 1 + \Psi - \theta_\nu \qquad (9)$$

Substituting for θ_1 from Eq. (9) into Eq. (8) gives

$$\sum_i \frac{z_i + R_i}{\left[1 + \Psi - \theta_\nu + \theta_\nu K_i\right]}\left(K_i - 1\right) = \Phi\left(\theta_\nu\right) = 0 \qquad (10)$$

The derivative of this function with respect to θ_ν is

$$-\sum_i \frac{z_i + R_i}{\left[\left(1 + \Psi - \theta_\nu\right) + \theta_\nu K_i\right]^2}\left(K_i - 1\right)^2 = \Phi'\left(\theta_\nu\right) \qquad (11)$$

Using this derivative, the Newton-Raphson method can be used to find the roots of this nonlinear equation.

Example 1: Steady State Simulation of MTBE Reactive Flash

Consider the example of a reactive flash where Methyl Tertiary Butyl Ether (MTBE) is formed from isobutene and methanol in the presence of an inert compound n-butane.

$$\text{Isobutene} + \text{MEOH} \Leftrightarrow \text{MTBE}$$

There are four components in the system. Consider an isothermal, isobaric, reactive flash. Let us assume that the Wilson equation is used for calculating the liquid phase activity coefficients. The Wilson binary interaction parameters and the Antoine coefficients for this system can be found in Chen, *et al.*[2] A solution to this isothermal, isobaric, reactive flash problem can be found using the modified Rachford-Rice procedure outlined in the last section. A pseudo-code can be developed as given below.

- Enter the input conditions
- Start with an initial guess for liquid compositions
- Outer loop checks for the convergence of liquid mole fractions
- Give the initial guess for θ_ν
- Inner loop checks for the convergence of θ_ν
- Update liquid mole fractions using Eq. (7) with R_i and K_i at previous liquid mole fractions and θ_ν
- Terminate when the outer loop satisfies the convergence criteria of liquid compositions

If we were to use the following process conditions: feed composition (z_i) = [0.1569 (isobutene), 0.1555 (methanol), 0.1 (MTBE), 0.5876 (n-butane)], temperature = 370.4729 K, pressure = 1114300 Pa, feed flow rate = 100 mol/h, holdup = 30 mol, then the solution for θ_ν is 0.4873.

This means that 48.73% of the feed will leave the unit as vapor and the remainder will leave as liquid. This example can be used to further analyze the effect of pressure and temperature on the amount of vapor leaving the system. Figure 2 depicts the effect of pressure on the vapor leaving the system, and it can be seen that with increasing pressure the amount of vapor at the outlet decreases.

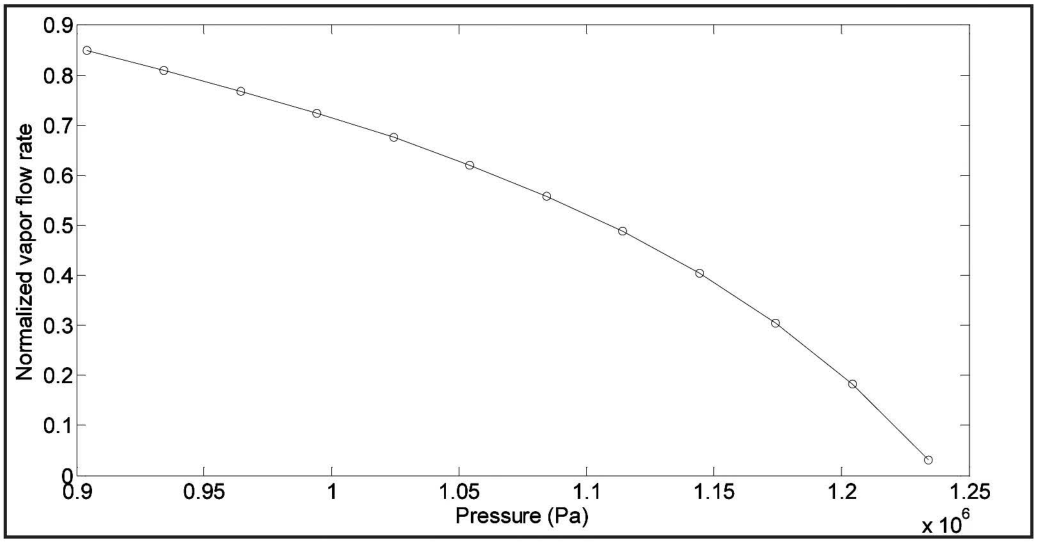

Figure 2. *Effect of pressure on the amount of vapor leaving the system.*

A similar analysis can be performed to study the effect of temperature on the vapor flow rate. Figure 3 depicts this relationship. In contrast to the pressure, with increasing temperature, the vapor flow rate actually increases.

2. DAE ANALYSIS OF THE REACTIVE FLASH PROBLEM

DAE systems involve both differential and algebraic constraints. The most general formulation for a DAE system is

$$\dot{x} = f(x, z, \lambda) \qquad (12)$$
$$0 = g(x, z, \lambda)$$

Some of the examples of DAE systems can be found in process control, chemical reaction engineering, separation process modeling, network modeling, and constrained body dynamics. DAE systems are characterized by the index of the system. The index of a DAE system is defined as the number of differentiations required to eliminate the algebraic terms, *i.e.*, to convert the DAE into an ordinary differential equation (ODE) system. A simple example of an index 2 DAE system is

$$\dot{y}_2 = y_1 + \lambda_1(t) \qquad (13)$$
$$0 = y_2 + \lambda_2(t)$$

Differentiating the algebraic equation once, we get

$$\dot{y}_2 = -\dot{\lambda}_2(t) \qquad (14)$$

Differentiating the algebraic equation twice [differentiation of Eq. (14)] yields

$$\ddot{y}_2 = \dot{y}_1 + \dot{\lambda}_1(t) = -\ddot{\lambda}_2(t) \qquad (15)$$

Putting these equations together we get an ODE as shown in Eq. (16).

$$\dot{y}_2 = y_1 + \lambda_1(t) \qquad (16)$$
$$\dot{y}_1 = -\dot{\lambda}_1(t) - \ddot{\lambda}_2(t)$$

Since the algebraic equation had to be differentiated twice to get to the ODE form, the above system is an index 2 system. There are differences in solving DAE systems for steady-state and dynamic behavior. The steady-state solution is simply achieved by solving all the equations with the differential part on the left-hand side (LHS) set to zero. The dynamic solution for the DAE system is more involved, however. One approach is to convert the DAE into an ODE through multiple differentiations as discussed above and to use a regular integration approach. This is not always advisable because it can be shown that the solution error in the algebraic constraint is proportional to the extent of index reduction. The error increases linearly if the index is reduced by one, quadratically if the index is reduced by two, and so on. It has to be ensured that the solution satisfies the original algebraic constraints at all times. The initial values have to satisfy the original constraint equation and also the new constraints generated through differentiation. This is called consistent initialization of the DAE system. A more detailed discussion on consistent initialization can be found in References 4-6. Some of the numerical integration and iterative methods for solving DAE systems are found in References 7 and 8.

These concepts can be taught effectively through the reactive flash example. Notice that the reactive flash example is a DAE system with n differential and (n+2) algebraic variables. This system can be simplified into just n differential variables and 2 algebraic variables system by direct substitution of equation (2b) into (2a) and writing equation (2d) in terms of the x_i variables. We chose to work with the original system to bring out the various aspects of the DAE systems in this article. Note also that this reduction is not always possible. In the general form of the DAE model given in Eq. (12), it might not be possible to write the algebraic equations as explicit functions of the differential variables.

The first exercise for the students would be to calculate the index of the reactive flash model, which is 2. This is because

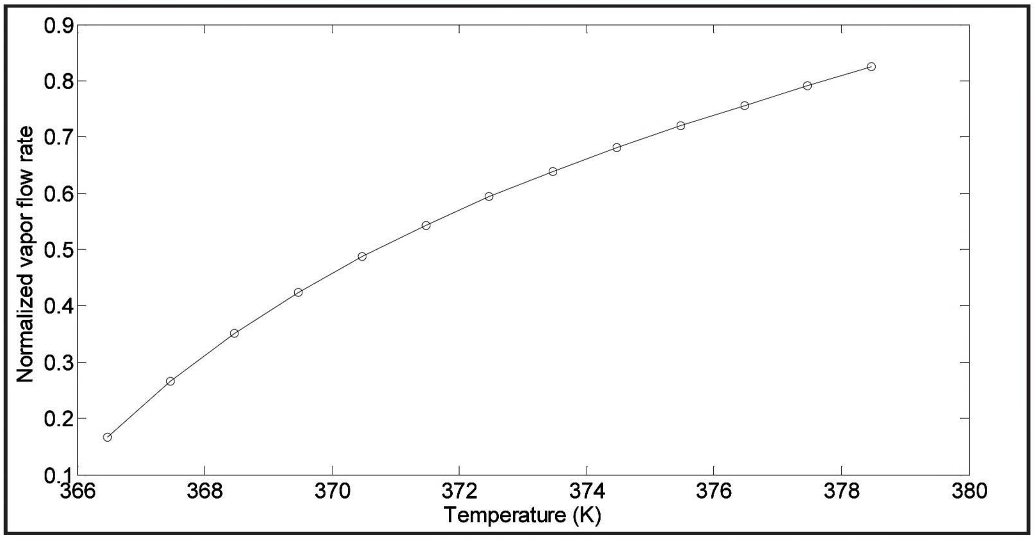

***Figure 3**. Effect of temperature on the amount of vapor leaving the system.*

the mole fraction summation equations have to be differentiated twice to get the differential ($\dot{\theta}_1$ and $\dot{\theta}_\nu$) terms. For solving the dynamic simulation problem, there are several possible approaches. The DAE system can be converted into an index 1 problem by differentiating the summation of liquid mole fractions and vapor mole fractions equations. The resulting DAE is of the form given in Eq. (17).

$$\begin{aligned} &\frac{dx_i}{d\tau} = z_i - \theta_1 x_i - \theta_\nu y_i + \frac{Da}{k_{ref}} \nu_i \varepsilon \text{ (17a)} \\ &y_i = K_i x_i \text{ (17b)} \\ &\sum \frac{dx_i}{d\tau} = 1 - \theta_1 - \theta_\nu + \frac{Da}{kref} \sum \nu_i \varepsilon = 0 \text{ (17c)} \\ &\sum \frac{dy_i}{d\tau} = \sum K_i \frac{dx_i}{d\tau} + x_i \frac{dK_i}{d\tau} = 0 \text{ (17d)} \end{aligned} \tag{17}$$

This is an index 1 DAE because one differentiation of Eq. (17b), (17c), and (17d) will lead to a regular ODE in all the (2n+2) variables, which is the original dimension of the system. This index 1 DAE can now be directly solved using the MATLAB ode15s routine. One has to ensure that consistent initialization of the variables is performed, however. Choosing the initial values of the (2n+2) variables such that equations (17b) – (17d) are satisfied will not yield a correct solution to the original problem. This is because when Eq. (2c) and (2d) are differentiated some information is lost. Eq. (17c) and (17d) will ensure that each summation of mole fractions equals a constant but not necessarily one. For consistent initialization, Eq. (2c) and (2d) should be added to Eq. (17b)-(17d), and this constrains the initial values. A generic criterion for when differentiating a subset of nonlinear DAE equations will further constrain the initial values can be found in Reference 4. If the reactive flash example is used in a postgraduate mathematical methods course, then the students can be asked to explore this aspect further. This model can also be used to look for singularities such as Hopf, branch, and limit points as discussed in Reference 9 and is another avenue for exploration in a postgraduate mathematical methods course.

For the reactive flash problem, the number of constraints to be satisfied by the initial values is equal to (n+4) and the number of initial values to be chosen equals (2n+2). The degrees of freedom equal (n-2). The reactive flash problem can be converted into ODE with the same number of variables (2n+2) or a reduced number of variables. In the following, the derivation of the reactive flash model with only differential equations in x_i is discussed. Eq. (17b) is eliminated from the set of equations by incorporating this equation directly into Eq. (17a). θ_1 and θ_ν appear explicitly in Eq. (17c). Performing algebraic manipulations on Eq. (17d) will also yield an equation that has θ_1 and θ_ν explicitly in it. Now these two equations can be solved simultaneously to explicitly write θ_1 and θ_ν in terms of the x_i variables. The final expressions for θ_1 and θ_ν are

$$\begin{aligned} \theta_i = &\left(\left(\sum_i \sum_j T_{ij} Z_j x_i + \sum_i \sum_j T_{ij} \frac{Da}{kref} \nu_j \varepsilon x_i + \sum_i K_i \left(Z_i + \frac{Da}{kref} \nu_i \varepsilon x_i\right)\right) - \left(\sum_i K_i K_i x_i + \sum_i \sum_j T_{ij} K_j x_j x_i\right)\left(1 - \frac{2Da\varepsilon}{kref}\right)\right) \\ &\div \left(\left(\sum_i \sum_j T_{ij} x_i x_j + 1\right) - \left(\sum_i K_i K_i x_i + \sum_i \sum_j T_{ij} K_j x_j x_i\right)\right) \end{aligned} \tag{18}$$

$$\begin{aligned} \theta_\nu = &\left(\left(\sum_i \sum_j T_{ij} Z_j x_i + \sum_i \sum_j T_{ij} \frac{Da}{kref} \nu_j \varepsilon x_i + \sum_i K_i \left(Z_i + \frac{Da}{kref} \nu_i \varepsilon x_i\right)\right) - \left(\sum_i \sum_j T_{ij} x_i x_j + 1\right)\left(1 - \frac{2Da\varepsilon}{kref}\right)\right) \\ &\div \left(\left(\sum_i K_i K_i x_i + \sum_i \sum_j T_{ij} K_j x_j x_i\right) - \left(\sum_i \sum_j T_{ij} x_i x_j + 1\right)\right) \end{aligned} \tag{19}$$

with the following definition

$$T_{ij} = \frac{\partial K_i}{\partial x_j} \tag{20}$$

The θ_1 and θ_ν expressions are substituted into Eq. (17a). Now Eq. (17a) with substitutions for the variables y_i, θ_1, and θ_ν is an ODE system [shown in Eq. (21)] that represents the dynamics of the reactive flash problem. The calculation of analytical derivatives is performed in the MAPLE environment. The equations generated in MAPLE are converted into a MATLAB function. The initial values are still constrained for the index 1 system that we discussed because the latest manipulations were algebraic with the same equations. Hence, for consistent initialization there are (n-2) degrees of freedom. In other words, for the ODE in the variables x_i, only (n-2) components can be specified and the remaining two mole fractions have to be solved to satisfy the constraints. This reflects the fact that the ODE resulted from a DAE and hence the initial states are constrained, unlike a pure ODE. Once consistent initialization is performed, the solution to the reactive flash problem can be obtained using any standard ODE solver, such as the ODE solver in MATLAB. The mole fractions that are computed will automatically solve the summation constraints.

The idea of Reactive Distillation can be explained to undergraduates through a simple reactive flash, which is an extension of the equilibrium flash problem. The reactive flash can be thought of as an idealization of a single stage in an RD column.

$$\frac{dx_i}{d\tau} = z_i - \theta_1\left(x_1 \ldots x_n\right)x_i - \theta_\nu\left(x_1 \ldots x_n\right)K_i\left(x_1 \ldots x_n\right)x_i + \frac{Da}{k_{ref}}\nu_i\varepsilon \quad \forall i \qquad (21)$$

Example 2: Dynamic Simulation of TAME Reactive Flash

Consider a reactive flash where Tertiary Amyl Methyl Ether (TAME) is synthesized by an acid catalyzed equilibrium reaction of isoamylenes and methanol. The reaction considered is

$$2M1B + 2M2B + 2MEOH \Leftrightarrow 2TAME$$

The reaction kinetics for TAME synthesis have been studied by various authors. Hwang, *et al.*,[10] used a concentration-based expression for combined etherification reactions from two isoamylenes. Later, rigorous kinetic studies were undertaken by Oost, *et al.*,[11] Christian, *et al.*,[12] and Sundmacher, *et al.*[13] These authors reported activity-based kinetic models for lumped as well as separate etherification reactions. In this example, the activity coefficients are calculated using a Wilson model. The Wilson binary interaction parameters and the Antoine coefficients were taken from Chen, *et al.*[14] Light gasoline fraction (C5-cut) from the fluidized catalytic unit is the source of isoamylenes. There are three isomers of amylene: 2 Methyl-1-Butene (2M1B) and 2-Methyl-2-Butene (2M2B), which are reactive, and 2-Methyl-3-Butene (2M3B), which is nonreactive. The reactive iso-amylenes are diluted with n-pentane as an inert solvent. The rate model used is taken from Chen, *et al.*[14]

There are five components in the system. Consider an isothermal, isobaric, reactive flash with the following conditions. In the data given below, the component feed compositions are provided in the order MeOH, 2M1B, 2M2B, TAME, and n-pentane.

Feed composition (z_i) = [0.2647, 0.0463, 0.2846, 0.0000, 0.4044]
Temperature= 335 K
Pressure=2.55 bar
Da =0.462

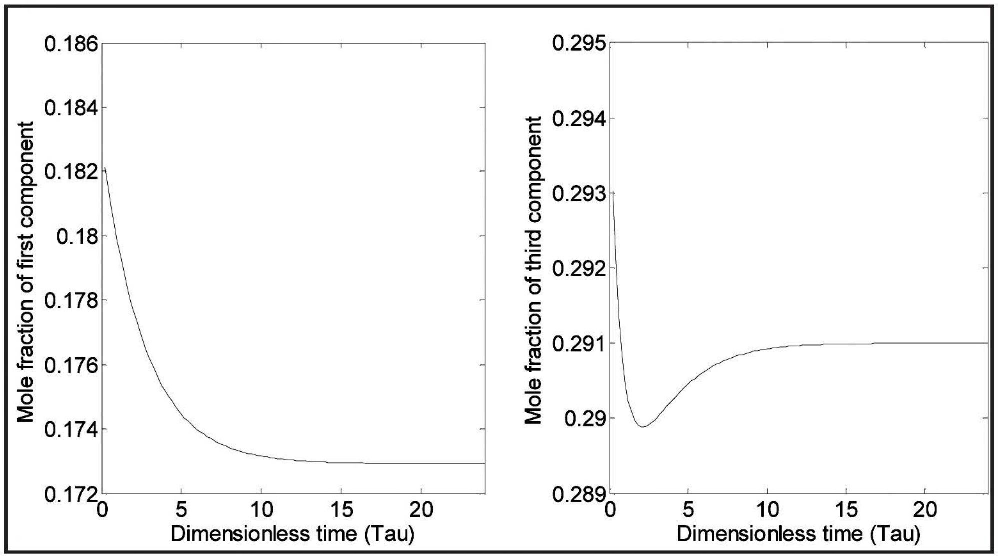

Figure 4. *Plots of first component and third component vs. dimensionless time (τ).*

For the dynamic simulation using the ODE, we need to choose consistent initial estimates. Since this is a five-component problem, the degrees of freedom equals 3 (5-2). Hence, we choose the three mole fractions in the liquid phase ($x_i(0)$) as [0.1828, 0.0303, 0.2944] and we get the other two mole fractions as [0.1131, 0.3794] for consistent initialization. These mole fraction values lead to $y_i(0)$ = [0.2561, 0.0359, 0.2789, 0.0174, 0.4117]. Notice that the mole fractions sum to one. The values for θ_l and θ_ν are 0.2720 and 0.6849, respectively. It is important to note that consistent initialization leads to the mole fractions summing to one, but does not automatically take care of the constraint that the mole fractions have to be non-negative. With this initialization, a dynamic simulation can be performed. The plots of the first component and the third component compositions against dimensionless time (τ) are shown in Figure 4. The numerical simulation results are shown in Table 1. In the first five columns of Table 1, the mole fraction values of the liquid at the outlet for the first 10 dimensionless time values are reported; the second-to-last column reports the mole fraction summation for the liquid, and the last column reports the mole fraction summation for the vapor. Notice that solving a consistently initialized ODE incorporates the mole fraction summation equalities at all values of the dimensionless time. The same simulation is run with a different consistent initial estimate: $x_i(0)$ = [0.1796, 0.0298, 0.2892, 0.1138, 0.3876]. The plots of the first and the third component compositions against dimensionless time (τ) using this initial value are shown in Figure 5. It is clearly evident from Figures 4 and 5 that the same steady state is reached, even though the initial values for these simulations are different.

TABLE 1

The mole fractions of five components in liquid phase and the summation of mole fractions in liquid phase and vapor phase for the first 10 instances.

Dimensionless Time(τ)	x_1	x_2	x_3	x_4	x_5	Σx	Σy
0.2	0.1821	0.0290	0.2930	0.1132	0.3827	1.0000	1.0000
0.4	0.1815	0.0280	0.2920	0.1132	0.3853	1.0000	1.0000
0.6	0.1809	0.0273	0.2913	0.1132	0.3872	1.0000	1.0000
0.8	0.1804	0.0269	0.2908	0.1132	0.3887	1.0000	1.0000
1.0	0.1798	0.0266	0.2905	0.1132	0.3899	1.0000	1.0000
1.2	0.1793	0.0263	0.2902	0.1133	0.3909	1.0001	1.0000
1.4	0.1789	0.0262	0.2901	0.1133	0.3917	1.0001	1.0000
1.6	0.1785	0.0261	0.2900	0.1133	0.3923	1.0001	1.0000
1.8	0.1781	0.0260	0.2899	0.1133	0.3929	1.0001	1.0000
2.0	0.1777	0.0259	0.2899	0.1132	0.3933	1.0001	1.0000

The dynamic solution starting with a non-steady state condition can be summarized as follows

- Identify the index of the DAE system
- Reduce the given DAE system to index 1 or ODE form
- Find the degrees of freedom, which is the difference between the total number of variables and the total number of algebraic equations
    - Perform consistent initialization by specifying the number of initial values equal to the degrees of freedom and the other values that are obtained from the solution to the algebraic constraints
    - Once initial values are specified, solve the ODE or index 1 DAE using an appropriate solver

3. CONCLUSIONS

In this paper, the introduction of DAE systems in the undergraduate curriculum is proposed through an interesting chemical engineering example, the equilibrium reactive flash. This is a reasonably simple example that is easy to understand both physically and mathematically. It is shown that this simple example can be used to teach the concepts of index and consistent initialization that are relevant in solutions to DAE systems. This example can be introduced in an undergraduate thermodynamics or mathematical methods class. Further, other options for deeper investigation into DAE systems, starting with the same example,

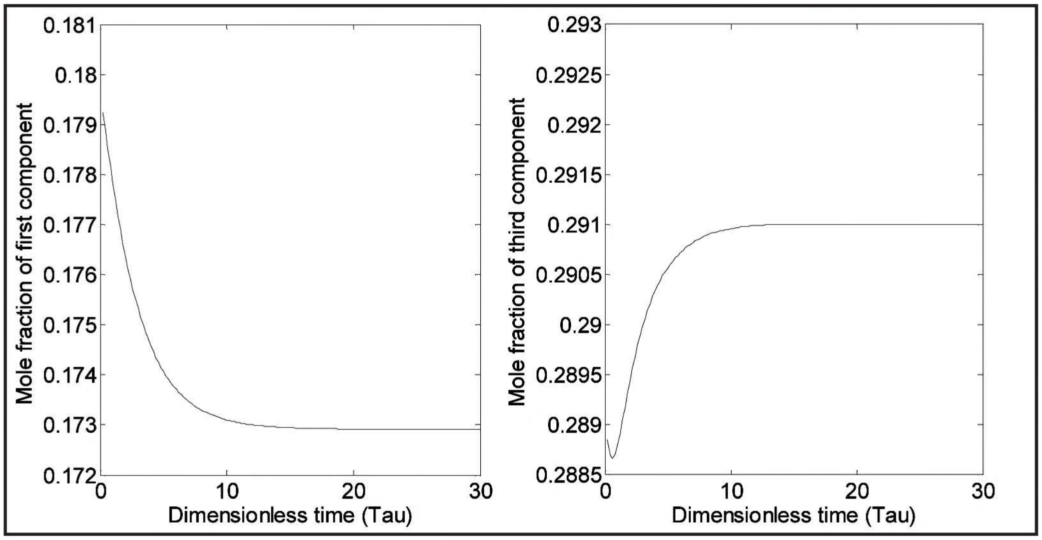

Figure 5. Plots of first component and third component vs. dimensionless time (τ).

are also pointed out if this material were to be included in a postgraduate mathematical methods course.

AVAILABILITY OF MATERIAL FOR USE IN CLASSROOM

The MATLAB codes used in this article can be obtained by contacting Dr. Rengaswamy at raghu.rengasamy@ttu.edu.

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