ChE *class and home problems*

The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu) or Mark A. Burns (e-mail: maburns@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

DYNAMIC AND STEADY-STATE BEHAVIOR OF A CSTR

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Mathematical models describe real systems in terms of a set of mathematical equations (differential or algebraic). This representation of the physical and chemical phenomena governing the system, along with the analytical and/or numerical solutions developed, enables us to predict the dynamic and/or steady-state behavior of this system. Analytical solutions are usually the most satisfactory, but they become difficult with increasingly complex systems. Numerical solutions are useful when analytical solutions cannot be obtained or when comparison with the available analytical solution is required to confirm the correctness of the latter.

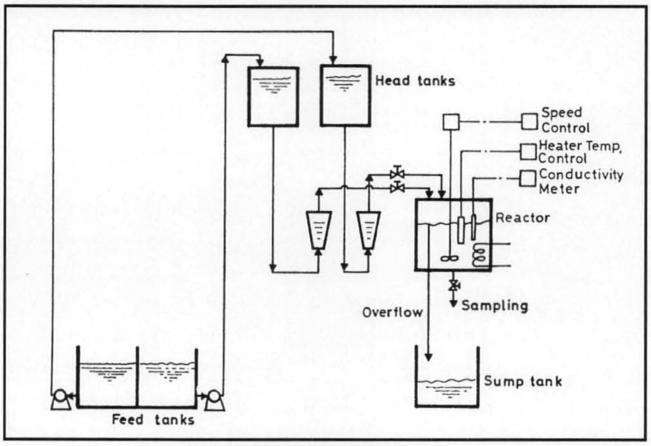
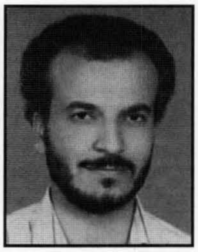


***Figure 1.** Reactor setup.*

Abu-Khalaf[1] described a reactor setup (see Figure 1) where a second-order reaction was studied with equimolar feed concentrations and equal flow rates of the reactants under isothermal conditions. Three stages of the CSTR were modeled, namely from beginning to overflow (*e.g.,* while the reactor is filling up to a constant volume), from overflow to the approach to steady state, and the final steady-state operation. Mathematical models with both analytical and numerical solutions were developed. The mathematics involved, however, is rather advanced, and students at this stage may not be familiar with Bessel functions and other advanced techniques. The mathematics can be simplified if a *first-order* reaction is studied instead of a second-order reaction.

A great many reactions follow first-order kinetics or pseudo first-order kinetics over certain ranges of experimental conditions.[2] Examples are the gas-phase decomposition of sulfuryl chloride, the radioactive disintegration of unstable nuclei, the hydrolysis of methyl chloride, CH_3Cl, the isomerization of cyclopropane to propenes, and the decomposition of dimethyl ether. A representative liquid phase chemical reaction, which can easily be followed, is the reaction between acetic anhydride and water. This is a first-order reaction with rate constant of 0.16 min^{-1} at room temperature. Using this as a model, the following problem is suggested.



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PROBLEM

Given the same setup as described above (Figure 1) and considering a first-order reaction under the same conditions, perform the following:

1. Develop mathematical models to describe the three stages mentioned above.
2. Solve the models both analytically and numerically.
3. Considering the differential equation and the final solution describing stage one, show how to circumvent the difficulty of defining the initial condition.

SOLUTION

Stage 1

During this stage, the reactor is filling up and the contents are still below the overflow level. This means that both the concentration and the volume are changing with time. A component mass balance gives

rate of accumulation = rate of input - rate of consumption

Therefore

$$\frac{d}{dt}(VC) = FC_0 - VkC \tag{1}$$

or

$$V\frac{dC}{dt} + C\frac{dV}{dt} = FC_0 - VkC \tag{2}$$

but $V = Ft$ (by total mass balance, assuming constant density and flow rate and noting that at $t = 0$, $V = 0$). Equation (2) becomes, after some manipulation

$$\frac{dC}{dt} + \left(\frac{1}{t} + k\right)C - \frac{C_0}{t} = 0 \tag{3}$$

Equation (3) is a linear first-order differential equation, which can be solved by the integrating factor method. The integrating factor in this case is $t\exp(kt)$, and the final solution is

$$C = \frac{C_0}{kt}\left[1 - \exp(-kt)\right] \tag{4}$$

Note here that application of the initial condition has to follow physical sense, *e.g.,* at $t = 0^+$, $C = C_0$. This difficulty will be obvious in the numerical solution.

Regarding the final solution, the exponential term can be written in a series form as $\exp(-kt) \approx 1 - kt$, and upon substituting this into Eq. (4), it is easily shown that as time approaches zero, $C = C_0$.

Another approach to model this stage is working with the number of moles, N, of reactant in the reactor at any time. A molal balance gives

$$\frac{dN}{dt} = -kN + FC_0 \tag{5}$$

The final solution (note that at t=0, N=0) is

$$N = \frac{FC_0}{k}\left[1 - \exp(-kt)\right] \tag{6}$$

Stage 2

In this stage the volume is constant, but the concentration is still changing with time because the process, although continuous, is not yet steady. A component material balance gives

$$\text{rate of accumulation} = \text{rate of input} - \text{rate of output} - \text{rate of consumption}$$

or

$$V\frac{dC}{dT} = FC_0 - FC - kVC \tag{7}$$

and therefore

$$\frac{dC}{dT} = \frac{C_0}{\tau} - \frac{C}{\tau} - kC \tag{8}$$

where

$T = t - \tau =$ time in minutes

$\tau = V/F =$ time constant

Again, Eq. (8) is a linear first-order differential equation, which can be solved by the integrating factor method; the integrating factor in this case is $\exp\left(\frac{1}{\tau} + k\right)T$. The final solution is

$$C = \frac{C_0}{\tau A}\left[1 + \left(\frac{C_1\tau}{C_0}A - 1\right)\exp(-AT)\right] \tag{9}$$

where $A = (1/\tau) + k$, and C_1 is the concentration at the beginning of stage two (at $t = \tau$).

Stage 3

In this stage, steady state prevails. Modeling of this stage can be approached either by simplifying Eq. (9) as $T \to \infty$ or by a component mass balance. Both will give, after some manipulation

$$C_s = \frac{C_0}{1 + k\tau} \tag{10}$$

NUMERICAL SOLUTION

The initial value problems (Eqs. 3 and 8) can be solved by a suitable Runge-Kutta subroutine (*e.g.,* IVPRK or DIVPRK from IMSL). Note that the initial condition for stage two is that $C = C_1$ at $T = 0$ (or $t = \tau$), where C_1 is the concentration at the end of stage one. The application of the initial condition to Eq. (3), when solving it numerically, may cause some confusion. Here we have to give a specific value at zero time, but at zero time Eq. (3) is not defined mathematically. This should not cause any difficulty if we consider the approach to t=0 rather than at t=0 itself. Thus, by considering the definition of a derivative, the two terms in Eq. (3) with time in the demonimator can be rewritten as time approaches zero as

$$\lim_{t \to 0} \frac{C - C_0}{t} = \left(\frac{dC}{dt} \right)_{t=0^+}$$

Thus, the limiting form of Eq. (3) as time approaches zero is

$$\left(\frac{dC}{dt} \right)_{t=0^+} = -\frac{1}{2} kC_0 \tag{11}$$

which can then be used to start the numerical solution.

DISCUSSION

Startup is one of the interesting points of the system shown in Figure 1. The way we start up the system will affect the derivation and behavior of the model. In our case, for example, the reactor is initially empty, and thus we have to care about the definition of the initial conditions. Thus, we say that at t = 0, V = 0, but as $t \to 0^+$, $C = C_0$. This is important when one has to deal with Eq. (4) and its differential form, Eq. (3), but not with Eq. (6) because initially the number of moles is zero. But we measure the concentration and not the moles, so if we express the number of moles in terms of concentration, we will arrive at the same difficulty as above. It will be an interesting point if one considers the startup with a known volume and concentration of the reactant. I strongly encourage the students to try this and note the difference.

The analytical and numerical profiles, which describe the dynamic and steady-state behavior of the CSTR, are shown in Figure 2 for kV/F = 2.5. The two profiles agree, confirming the correctness of the analytical solutions. In Figure 3, the effect of the parameter kV/F is shown. This parameter can be affected by a change in flow rate and/or a change in temperature since, usually, the volume of the reactor is constant. In our case, temperature is constant at 25 °C (where $k = 0.16\ \text{min}^{-1}$), the molar feed concentration = 10.5 M, and V = 3.8 l; thus the change in kV/F is affected by the change in F only. As can be seen, the approach to steady state is faster for lower values of kV/F. Shown in the figure are the limits of the three stages for the case of kV/F = 3.0. This makes the comparison easier for the other two cases where the time constant can be calculated from the data given above.

The mathematics involved here is simpler than it would be with higher orders of reaction, and because of this students will enjoy the process of modeling and will, hopefully, gain the courage and experience to tackle more complicated problems.

ACKNOWLEDGMENT

The author wishes to acknowledge helpful discussion and suggestions by the editors of the "Class and Home Problems" section and the reviewers of this article.

NOMENCLATURE

C	concentration of the reactant at any time in mols/liter
C_0	concentration of the reactant in feed, mols/liter
C_1	concentration at the end of stage one, mols/liter
F	total flow rate, liter/min
k	reaction rate constant, min^{-1}
N	number of moles of reactant at any time, moles
t	time, min
T	time for stage two, min
V	volume of the reacting system, liter
τ	time constant, min

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1. Abu-Khalaf, A.M., *Chem. Eng. Ed.,* **28**(1), 48 (1994)
2. Hill, G.C., *An Introduction to Chemical Engineering Kinetics and Reactor Design,* 1st ed., John Wiley, New York, NY (1977) ❒

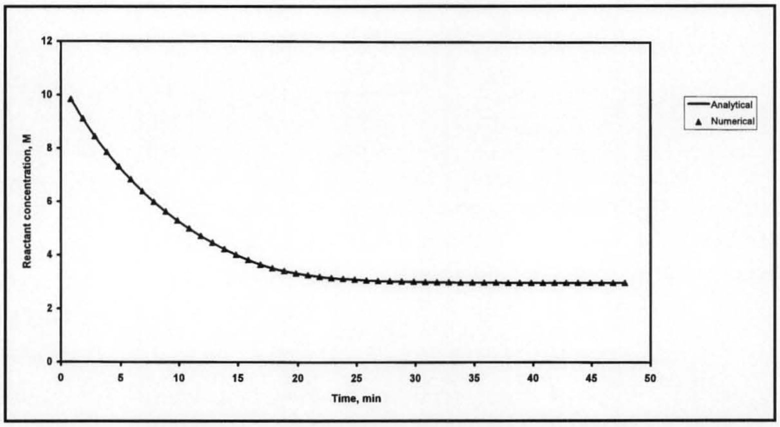

Figure 2. *Analytical and numerical profiles.*

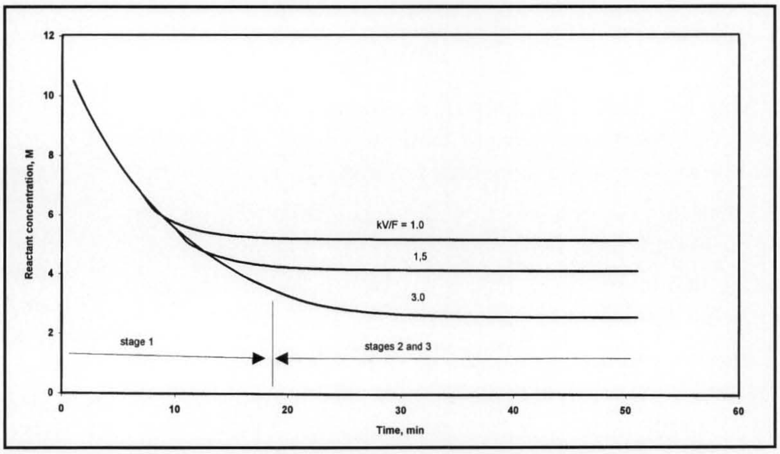

Figure 3. *Analytical solution as compared to different values of kV/F.*