

# MATHEMATICAL MODELING OF AN EXPERIMENTAL REACTION SYSTEM

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Usually, one objective of a laboratory experiment is measuring the values of a dependent variable as it changes with an independent variable, or determining the values of some characteristic constants or parameters of a system. It is also useful to teach the students how to build up a mathematical model of the system under investigation and to think of possible analytical or numerical solutions to the model.

Models which describe the transient period of the system (e.g., start-up or shut-down) contain differential equations which can be solved either analytically or numerically (if the model is relatively complex). Steady-state models (with uniform dependent variables) usually contain algebraic equations.

The objective of this paper is to simulate the dynamics of a CSTR during different stages of its continuous operation. Mathematical models will be developed, along with analytical and numerical solutions, and together, these will be compared with experimental results.

## A CLASSICAL EXPERIMENT

The reaction between ethyl acetate and sodium hydroxide in aqueous solutions is demonstrated in many chemical engineering labs. It is characterized by its constant density, and it is safe and easy to operate and analyze. The reaction rate is

well established, and the mechanisms have been discussed in detail. The overall reaction rate is regarded as a second-order reaction, particularly at low temperatures.<sup>[1-3]</sup>

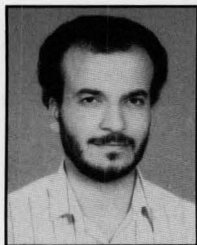
In this study, the experiment is operated batchwise to determine the order of the reaction and the reaction-rate constant. These kinetic data are used to simulate the dynamics of the continuous mode operation.

## SET-UP AND PROCEDURE

The saponification of ethyl acetate occurs quickly, so it is more convenient to measure the concentration by following the change in conductivity than to titrate aliquots since the latter need sampling, quenching (to stop the reaction in the sample), and back-titration.

In a batchwise mode and at zero time, one liter of sodium hydroxide (0.1 N) and one liter of ethyl acetate (0.1 N) are thoroughly mixed at room temperature (23°C). The conductivity is recorded at suitable intervals of time, and the concentration can be read from a suitable calibration curve. The order of the reaction and the rate constant can be deduced from these batchwise data by a suitable differential and/or integral analysis. Both methods give a second-order and a reaction-rate constant,  $k = 6.1 \text{ l/mol}\cdot\text{min}$ .

Continuous operation, which is the objective of this study, is illustrated in Figure 1. Solutions of sodium hydroxide and ethyl acetate (at equal concentrations) are pumped first to the head tanks (to eliminate fluctuations in flow rate caused by direct pumping to the reactor) and then to the reactor at suitable, but equal, flow rates. The speed of the stirrer is adjusted by the stirrer speed control, while temperature control is achieved through the heater temperature control and the cooling coil. The conductivity is recorded at suitable intervals of time. Notice that at zero time the reactor is empty. During the startup and filling of the reactor, both concentration and volume change with time until the reactor overflows; then the concentration will change with time until steady state is reached.



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## MATHEMATICAL MODELS AND ANALYTICAL SOLUTIONS

Once students determine the order of reaction and the rate constant from the batch data and become familiar with the system, they are in a position to mathematically model and develop a transient analysis of the *continuous* mode operation of the stirred reactor. Three stages can be modeled:

1. From beginning to overflow
2. From overflow to steady state
3. Steady state operation

Obviously, the first and second stages are transient, while stage three is represented by a steady-state model. In this study, analysis is restricted to identical concentrations and flow rates of reactants. We let

- $C$  = molar reactant concentration in the reactors; mols/liter  
 $C_0$  = molar reactant concentration in feed; mols/liter (M)  
 $F$  = flow rate; liter/min  
 $k$  = reaction rate constant; liter/mols·min  
 $r = kC^2$ , the rate of reaction; mols/min·liter  
 $t$  = time; min  
 $V$  = volume of the reacting system; liter

### Stage One

This stage is semibatch. There is no output because the reactor contents do not yet reach the overflow level. A material balance on either NaOH or ethyl acetate (both reactants are at the same concentration and flow rate) gives:

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

Therefore

$$\frac{d}{dt}(VC) = FC_0 - VkC^2 \quad (1)$$

or

$$V \frac{dC}{dt} + C \frac{dV}{dt} = FC_0 - VkC^2 \quad (2)$$

But  $V$  is a function of time, and since the system is of constant density and flow rate, a total mass balance gives

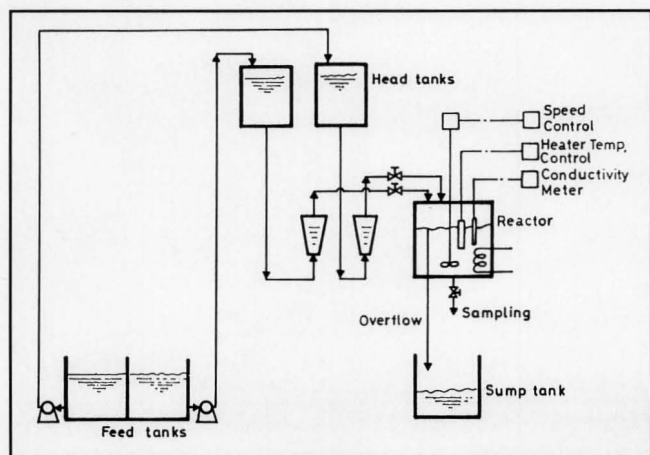


Figure 1. Reactor set-up

**Once students determine the order of reaction and the rate constant from the batch data and become familiar with the system, they are in a position to mathematically model and develop a transient analysis of the continuous mode operation of the stirred reactor.**

$$\frac{dV}{dt} = F \quad \text{or} \quad V = Ft$$

since at  $t = 0$ ,  $V = 0$ . Equation (2) then becomes

$$Ft \frac{dC}{dt} + CF = FC_0 - FtkC^2$$

or

$$\frac{dC}{dt} = \frac{C_0}{t} - \frac{C}{t} - kC^2 \quad (3)$$

Equation (3) is subject to  $C = C_0$  at  $t = 0$ . This equation can be solved using the substitution

$$u = \exp\left(k \int C dt\right)$$

Equation (3) becomes, after some manipulation,

$$t^2 \frac{d^2u}{dt^2} + t \frac{du}{dt} - kC_0tu = 0 \quad (4)$$

which can be solved via Bessel functions by using the substitution  $z = t^{1/2}$ . Equation (4) becomes

$$z^2 \frac{d^2u}{dz^2} + z \frac{du}{dz} - 4kC_0z^2u = 0 \quad (5)$$

which is a modified Bessel equation, the general solution of which (in terms of  $t$ ) is<sup>[4]</sup>

$$u = AI_0(\sqrt{4kC_0t}) + BK_0(\sqrt{4kC_0t}) \quad (6)$$

where  $I_0$  and  $K_0$  are the modified Bessel functions of the first and second kind of order zero, respectively, and  $A$  and  $B$  are constants to be determined by the boundary conditions and the nature of the problem.

At this point, students can be asked to carry out several interesting exercises:

1. Perform the steps required to get Eqs. (4) and (5).
2. At  $t = 0$ ,  $u = 1$ , greatly simplifying Eq. (6). Show that  $B$  must vanish.
3. We are looking for a relation between  $C$  and  $t$ ; thus Eq. (6) should be written in terms of  $C$ .
4. If task 3 above is performed, it can be shown that

$$C = \sqrt{\frac{C_0}{kt}} \frac{I_1(2\sqrt{kC_0t})}{I_0(2\sqrt{kC_0t})} \quad (7)$$

where  $I_1$  is the modified Bessel function of the second kind of order one. This equation shows that  $C$  is not defined at  $t = 0$ , although at this initial time  $C = C_0$ . It is a good exercise for the students to show that this condition is implicitly

satisfied by expanding the modified Bessel functions, considering only the first few terms.

### Stage Two

The second stage is continuous, but not yet steady. The concentration is changing with time but the volume of the reactants is constant. A material balance takes the form:

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

or

$$V \frac{dC}{dT} = FC_0 - FC - kVC^2 \quad (8)$$

and therefore

$$\frac{dC}{dT} = \frac{C_0}{\tau} - \frac{C}{\tau} - kC^2 \quad (9)$$

where

$$T = t - \tau = \text{time in minutes}$$

$$\tau = V/F = \text{time constant}$$

At steady state,  $C = C_s$ , which is a particular solution to Eq. (9). Substituting

$$C = C_s + \frac{1}{Z} \quad (10)$$

changes Eq. (9) to a linear first-order differential equation which can be solved by the integrating factor method. The final solution is

$$C - C_s = \frac{1}{\left(B \exp(AT) - \frac{k}{A}\right)} \quad (11)$$

where

$$A = \frac{1}{\tau} + 2kC_s$$

$$B = \frac{1}{C_1 - C_s} + \frac{k}{A}$$

and  $C_1$  is the concentration at the beginning of stage two (e.g., at  $t = \tau$ ).

Students can be asked to derive Eq. (11) by starting from Eqs. (9) and (10). It is interesting to check Eq. (11) at  $T = 0$  and at steady state (e.g., as  $T \rightarrow \infty$ ) and to think of a special form of the equation suitable for short times.

### Stage Three

This is the easiest stage to model. A material balance requires that

$$\text{rate of input} = \text{rate of output} + \text{rate of consumption}$$

or

$$FC_0 = FC + Vr \quad (12)$$

Therefore

$$FC_0 = FC_s + kVC_s^2$$

and

$$k\tau C_s^2 + C_s - C_0 = 0 \quad (13)$$

where  $C_s$  is the steady state concentration. If  $k$  is known,  $C_s$  can be predicted, or if  $C_s$  is measured,  $k$  can be calculated.

Notice that Eq. (13) can be derived directly from Eq. (9) where at steady state  $dC/dT = 0$  and  $C = C_s$ .

## NUMERICAL SOLUTIONS

Numerical solutions are required whenever analytical solutions are not possible or are difficult to obtain. A suitable Runge-Kutta subroutine (e.g., IVPRK or DIVPRK from IMSL) can be used to solve the initial value problems, Eqs. (3) and (9). Concentrations from Eq. (7) can be calculated using IMSL special functions (DBSI0 and DBSI1). Equation (3) is not defined at  $t = 0$ , but it can be shown (by Taylor series expansion) that

$$\left(\frac{dC}{dt}\right)_{t=0} = -\frac{1}{2}kC^2$$

This condition should be considered in the numerical solution. Notice that the initial condition for stage two is that  $C = C_1$  and  $T = 0$  (or  $t = \tau$ ), where  $C_1$  is the concentration at the end of stage one.

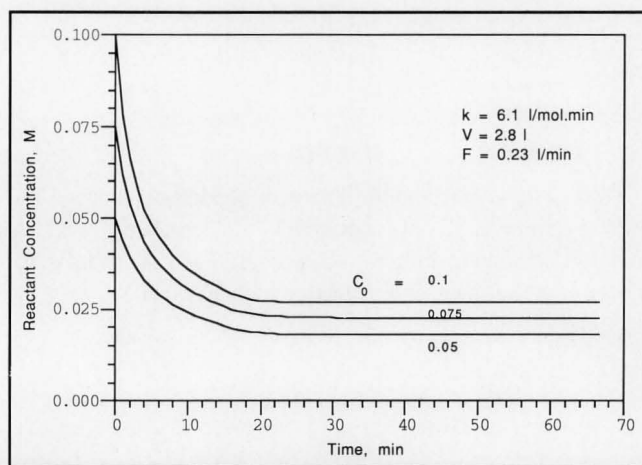


Figure 2. Analytical and numerical profiles (perfectly matched) of reactant concentration for different initial concentrations.

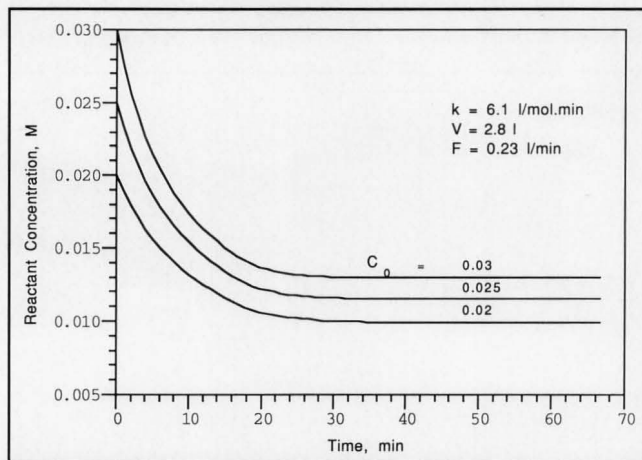


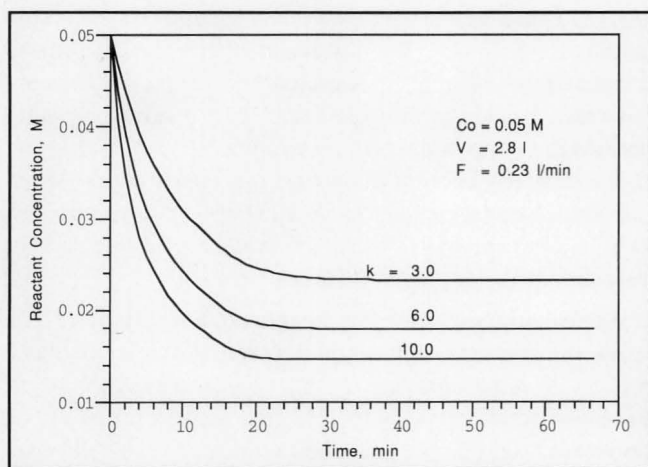
Figure 3. Analytical and numerical profiles (perfectly matched) of reactant concentration for different initial concentrations.

Equations (3) and (9) were solved numerically and the solutions were compared to the analytical solution from Eqs. (7) and (11). Figures 2, 3, and 4 show these theoretical profiles for different cases of initial concentrations and for different values of rate constant ( $F = 0.23$  l/min,  $V = 2.8$  l). Notice that both numerical and analytical profiles coincide, *i.e.*, they match perfectly. Both the analytical and the numerical solutions are compared to experimental results (shown in Figure 5) for the case of 0.1 N initial concentration, a volume of reactants of 2.5 l and a total flow rate of 0.24 l/min.

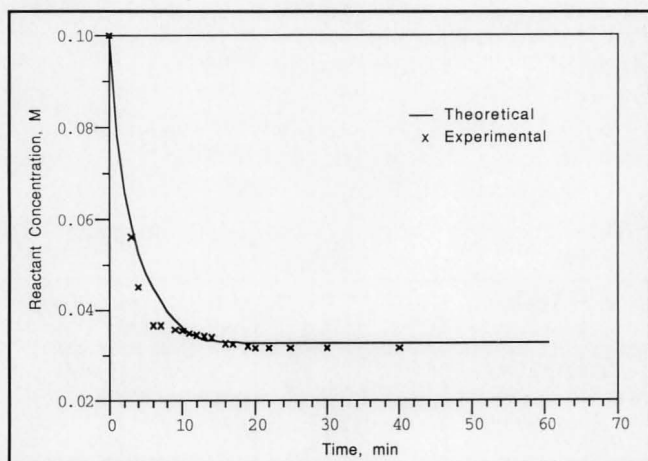
## DISCUSSION

Continuous operation of the CSTR setup as shown in Figure 1 can serve several useful functions:

1. It can foster a realization of some practical problems, such as fluctuations in flow. A possible remedy is the use of head



**Figure 4.** Analytical and numerical profiles (perfectly matched) of reactant concentration for different rate constant values.



**Figure 5** Theoretical profile of reactant concentration as compared to experimental results. ( $C_0 = 0.1$  M,  $V = 2.5$  l,  $F = 0.24$  l/min).

(gravity) tanks. This could serve as a practical design problem.

2. It can spur students to think of start-up procedures that achieve efficient transient operations, *e.g.*, how to introduce the reactants into the vessels, and when and how to heat (or cool), if necessary.
3. It can encourage development of reliable mathematical models that describe the performance of the continuous system. This reliability should be checked against experimental data and reasons for any discrepancies between theory and experiment should be discussed.

Theoretical performance of the continuous mode operation is shown in Figures 2, 3, and 4. There is almost no difference between numerical and analytical solutions, as can be clearly seen from the figures. They match perfectly. This confirms the correctness of the analytical solutions.

Both solutions are compared with experimental results, as shown in Figure 5. A discrepancy between theoretical and experimental results is noticed in the initial period of the start-up operation. It is not difficult to predict, theoretically, the concentration at any time, but limitation of solutions in the reactor at the beginning of the start-up makes it difficult to accurately measure the concentration. Stirring during this initial period causes air bubbles, and this will affect the performance of the conductivity meter. A possible solution to this problem is to increase the flow rate (in new runs) or to measure the concentration using other means. Students should think of possible limitations to these solutions.

Students will find it interesting to consider the possible reasons for this discrepancy. They should first think of experimental errors and then check the assumptions of the model in order to think of new models, if they are required. They will quickly come to a realization of the difference between models and reality.

Another interesting point is the approach to steady state concentration. As can be seen from the figures, a steady state condition is approached asymptotically. Thus, depending on the significant figures required by the experiment, different values of experimental steady-state concentrations can be recorded, and they will represent a percentage of the theoretical steady-state value which can be achieved from stage three by using Eq. (13).

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