A First Course on Kinetics and Reaction Engineering
Unit 19. Analysis of Batch Reactors

Overview

As noted in Unit 18, batch reactor processing often follows an operational protocol that involves sequential steps much like a cooking recipe. In general, each step in the operational protocol must be analyzed separately. Unit 19 describes and illustrates how to quantitatively analyze a step in the operational protocol using the batch reactor design equations that were derived in Unit 17. In particular, Unit 19 discusses which of the mole and energy balances are needed to accurately model different types of processing steps. It also describes how to identify zero-valued and insignificant terms that can be dropped from the design equations. Finally, it considers a few of the more common ways of modeling heat transfer between the reactor contents and either a submerged heat transfer coil or an external heat transfer jacket.

Learning Objectives

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- Heat transfer with a constant temperature heat transfer fluid
- Latent heat change for a two-phase heat transfer medium
- Perfectly mixed, single phase heat transfer fluid energy balance

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Recognize problems wherein the reactor can be modeled as a perfectly mixed batch reactor
- Formulate the batch reactor design equations for any step in the operating protocol of a specified batch reactor system
- Noting that the elapsed time is the independent variable, classify every other quantity in the batch reactor design equations as a dependent variable, a variable other than a dependent variable or a constant
- Solve the batch reactor design equations for any step in the operating protocol of a specified batch reactor system, and use the results to perform requested reaction engineering tasks

Information

In a reaction engineering analysis, the reactions that take place are known, as are the corresponding rate expressions. The objectives are (i) to construct an accurate mathematical model of the reactive process and (ii) to use that model to perform some engineering task. In a batch reactor, the reactive process begins once all of the reagents have been charged to the reactor and the inlet (and outlet) valves have been closed. In general, the reactive process is carried out in a series of steps which will be referred to here as the operational protocol. Each step in the operational protocol is typically modeled separately. The final conditions of one step become the starting conditions of the next. For present purposes, we are interested in modeling any one step in the operational protocol. While a

systematic approach will be offered here, one must recognize that not every problem is the same, and at times, it will be necessary to adapt the approach described here to the problem at hand.

It is a good idea, at the very start of the analysis to convert all known quantities to a consistent set of units. That is, pick units for mass, temperature, pressure, volume, time, etc. and convert all known quantities to the appropriate combination of the selected units. At the same time, each quantity can be examined to determine whether it is extensive or intensive. If every known quantity is intensive, then a value can be selected for any one extensive quantity and used as the basis for the calculations.

The next step is to formulate the design equations for the step being modeled. In general, the design equations will consist of an energy balance and one or more mole balances on the reacting fluid along with an energy balance on the heat transfer medium (e. g. cooling water in the reactor jacket or a submerged cooling coil). In some cases, one or more of these equations may not be needed, however.

Consider the mole balance design equations; a mole balance for any one species, i, is given in equation (19.1). There is no need to write mole balances for species that are neither a reactant nor a product in any of the reactions. Species like this can be referred to as inerts, and since they do not participate in any of the reactions, the number of moles of each inert is a constant. At the minimum the number of mole balance design equations must equal the number of mathematically independent equations. When this minimum number of mole balance design equations is used, the moles of each of the species for which a mole balance *was not written* must be computed using the extent of reaction or a mole table. It is permissible to use more than the minimum number of mole balances. For this course, where the number of reactions will always be relatively small, it is recommended that whenever possible, a mole balance design equation be written for every species except the inerts. When this is done, it is no longer necessary to use a mole table or the extent of reaction to calculate the moles of any species; they are found directly by solving the design equations.

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j \tag{19.1}$$

Next consider the energy balance design equation given in equation (19.2); it represents an energy balance on the reacting fluid. The first important point to recognize is that whenever the operational step being analyzed is isothermal, the energy balance and the mole balances are mathematically decoupled. In other words, *when a batch reactor operational step is isothermal, the mole balances can be solved independently from the energy balance*. Thus, if the problem being solved only requires knowledge of the composition during the processing step, equation (19.2) is not needed. Most real-world reaction engineering tasks will require knowledge of both the composition and thermal quantities, but many textbooks and standardized tests feature problems involving an isothermal reactor where the energy balance is not needed to solve the problem.

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all \\ species}} \left(n_i \hat{C}_{p,i} \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt} \tag{19.2}$$

The shaft work term, $\dot{W}$, represents mechanical work done by the reacting fluid on the surroundings. Typically this kind of work involves a moving boundary, such as a fluid expanding and moving a piston. In most commercial batch reactors, the only shaft or moving boundary is an agitator that extends into the reacting fluid. The agitator is similar to a propeller; it is rotated rapidly causing the fluid to mix. The amount of work involved in doing this is virtually always negligible compared to the heats associated with chemical reactions. Therefore, unless special circumstances are noted (highly viscous fluid, reactor fitted with a moving piston, etc.) the work term can be set equal to zero.

Next consider the last two terms in equation (19.2) when the reacting fluid is an ideal gas mixture. Most commercial batch reactors are rigid vessels with a fixed internal volume, and the reacting gas will always occupy the entire internal volume. Therefore the volume of the reactor is equal to the reaction volume, and both are constant. If the reaction volume is constant then it's derivative with respect to time is equal to zero. Therefore, *when the reacting fluid is an ideal gas, the last term in equation (19.2) is always equal to zero*.

The pressure may change with time in a gas phase batch reaction as a result of temperature changes or changes in the total moles, as can be seen by examination of the ideal gas law. Therefore, *when the reacting fluid is an ideal gas, the derivative of the pressure with respect to time will be non-zero and given by equation (19.3)*. There are at least two ways to deal with the derivative of the pressure with respect to time. One is to leave it as it is in equation (19.2) and to add equation (19.3) as an additional design equation. The alternative, which will be the approach used in this course, is to substitute equation (19.3) for $\frac{dP}{dt}$ in equation (19.2). The resulting two terms containing $\frac{dT}{dt}$ can be combined, and the appropriate mole balance design equation, equation (19.1) can be substituted for each of the $\frac{dn_k}{dt}$ terms. This is illustrated in Example 19.2.

$$P = \frac{RT \sum\limits_{\substack{k = \text{all} \\ \text{species}}} n_k}{V} \qquad \Rightarrow \qquad \frac{dP}{dt} = \frac{R}{V}\left\{\left(\frac{dT}{dt} \sum\limits_{\substack{k = \text{all} \\ \text{species}}} n_k\right) + \left(T \sum\limits_{\substack{k = \text{all} \\ \text{species}}} \frac{dn_k}{dt}\right)\right\} \qquad (19.3)$$

Before considering the last two terms in equation (19.2) for reacting liquids, it is useful to recall that this formulation of the energy balance assumes the reacting fluid to be an ideal solution. This means that if one measured out the amount of each reagent present at the start of the reaction separately, including solvents and other non-reactive components, and then mixed them together, the sum of the internal energies of the separate reagents would equal the internal energy of the resulting solution. Similarly, the sum of the volumes of the separate reagents would equal the volume of the resulting solution. Put differently, it is assumed that there is no Δu of mixing and no ΔV of mixing when an ideal solution forms. However, even though there is no ΔV of mixing, *the volume of the ideal solution can change due to a change in composition, that is due to reaction*. That is, if one measured out the amount of each reagent present at the **end** of the reaction separately, including solvents and other non-reactive components, and then mixed them together, the sum of the volumes of the separate reagents would equal the volume of

the resulting solution. However, the volume of the ideal solution at the _end_ of the reaction need not be the same as the volume of the ideal solution at the _start_ of the reaction, even though there is no ΔV of mixing at either the start or the end of the reaction. The volume change is due to compositional change, not due to mixing.

In contrast to a gas phase solution, a batch reactor is almost never run with the reacting solution filling its entire volume. There is almost always a small volume at the top of the reactor that contains a vapor. The mole and energy balances for the batch reactor are actually balances on the reaction volume, in this case, the volume of the ideal solution, not the entire reactor volume. As a consequence, it is possible for the reaction volume to change, and so _generally, the derivative of the volume with respect to time need not equal zero when the reacting fluid is an ideal liquid solution and there is gas-filled headspace in the reactor_. Unfortunately, there isn't a simple equation of state like the ideal gas law that applies to ideal liquid solutions, and consequently there isn't a simple equation like equation (19.3) that can be used with ideal liquid solutions. In some cases, it may be possible to assume the density of the reacting ideal solution to be constant. _When the density of a reacting ideal liquid solution is assumed to be constant, the derivative of the volume with respect to time will equal zero_.

However, if the reaction volume does change, then there will be an equal and opposite change in the headspace volume because the total reactor volume is constant. If the headspace volume changes, then the pressure in the headspace will change as predicted by the ideal gas law. Indeed, the pressure in the headspace will also change if the temperature changes. If the pressure in the headspace changes, that will cause an equal change in the pressure in the liquid phase. The kinetics of most liquid phase reactions are not strongly affected by total pressure, so there is little advantage to an increase in the pressure. Indeed, the vessel walls, valves, etc. will all need to be designed to withstand the increased pressure, which will increase the cost of the reactor. Nonetheless, _generally, the derivative of the pressure with respect to time need not equal zero when the reacting fluid is an ideal liquid solution_.

To avoid the increase in pressure when an ideal liquid solution is reacting, a controller can be used to maintain a constant pressure. It does so by releasing gas from the headspace whenever the pressure starts to increase and by admitting gas to the headspace whenever the pressure begins to decrease. Note that the reactor is still a batch reactor because the headspace is not the reacting fluid; no material is added to or removed from the reacting ideal liquid, and as such, the reactor retains its batch character. In most instances in this course, when the reacting fluid is a liquid, it will be assumed that there is some amount of headspace in the reactor and that a controller is used to maintain constant pressure as just described. _When the reacting fluid is an ideal liquid solution and a constant pressure is maintained in the reactor headspace, the derivative of the pressure with respect to time will equal zero_.

Finally, consider the heat input term, $\dot{Q}$. _If the operational processing step being modeled is adiabatic (or equivalently, if the reactor is perfectly insulated), the heat input term is equal to zero_. Since the reaction volume is perfectly mixed, the temperature is uniform throughout the reaction volume. In most commercial batch reactors heat is transferred to or from a heat transfer fluid or heat transfer medium. The heat transfer fluid typically flows either in a jacket that surrounds the reaction volume or in a

coil of tubing that is submerged in the reaction volume. *If the temperature of the heat transfer fluid is uniform throughout either the reactor jacket or the submerged coil, the heat input term is given by equation (19.4)*, where T_e is the temperature of the heat transfer fluid (the "e" stands for "external" since this is the temperature external to the reaction volume), U is the appropriate overall heat transfer coefficient and A is the area of the wall through which the heat is conducted (either the jacket wall or the coiled tube wall).

$$\dot{Q} = UA\left(T_e - T\right) \tag{19.4}$$

There are three situations where the temperature will be essentially uniform throughout the heat transfer fluid. The first is where the heat transfer fluid supplies or removes heat by undergoing a phase change. The most common example would be where saturated steam flows into the coil or jacket where it condenses giving up its latent heat of vaporization. It then leaves as a liquid at the same temperature as the entering steam. In this case the heat input can be related to the minimum flow rate of the heat transfer fluid according to equation (19.5) where $\dot{m}_{min}$ denotes the minimum mass flow rate of the heat transfer fluid and $\Delta \tilde{H}_v\left(T_e\right)$ is the mass-specific latent heat of vaporization of the heat transfer fluid at temperature, T_e. To clarify, the amount of heat transferred from the heat transfer fluid to the reaction volume is fixed by equation (19.4). If the mass flow of heat transfer fluid is greater than $\dot{m}_{min}$, then only an amount equal to $\dot{m}_{min}$ will undergo phase change. If the mass flow of the heat transfer fluid is less than $\dot{m}_{min}$, then equation (19.4) will no longer be valid because the saturated heat transfer fluid is not able to provide that amount of heat. One would need to consult a heat transfer handbook and find an appropriate expression to replace equation (19.4), and one would need to use the proper heat transfer coefficient for that new expression.

$$\dot{Q} = \dot{m}_{min}\left(\Delta \tilde{H}_v\left(T_e\right)\right) \tag{19.5}$$

The second situation where the temperature will be uniform throughout the heat transfer fluid is when the heat transfer fluid may be assumed to be perfectly mixed. In this situation, the heat transfer fluid entering the jacket is at temperature, T_e^0, while the fluid leaving the jacket (as well as the fluid everywhere within the jacket) is at temperature, T_e. The temperature of the heat transfer fluid can be related to its flow rate through an energy balance on the heat transfer fluid. If the mass-specific heat capacity of the heat transfer fluid, $\tilde{C}_{p,e}$, is assumed to be constant, the energy balance on the heat transfer fluid takes the form given in equation (19.6), where ρ_e represents the (constant) density of the heat transfer fluid and V_e represents the total volume of heat transfer fluid within the jacket. In this situation, equation (19.6) shows that T_e can be made to change by changing the flow rate, $\dot{m}$, of the heat transfer fluid. Thus, by varying the flow rate of the heat transfer fluid, the amount of heat transferred to the reaction volume, equation (19.4), can be varied. *In the analysis of a processing step where the heat transfer fluid is assumed to be perfectly mixed, equation (19.6) must be solved simultaneously with the mole and energy balances on the*

reaction volume. In such situations, the flow rate of the heat transfer fluid can be specified to vary over time, and equation (19.4) should be substituted into both equation (19.2) and equation (19.6).

$$\dot{m}\tilde{C}_{p,e}\left(T_e^0 - T_e\right) - \dot{Q} = \rho_e V_e \tilde{C}_{p,e}\frac{dT_e}{dt}$$

(19.6)

A third situation where equation (19.4) might apply is when there is only a small change in the temperature of the heat transfer fluid between the inlet and outlet of a submerged heat transfer coil. In this case T_e would represent the average temperature of the heat transfer fluid within the coil. A good reference on heat transfer should be consulted in any situation where there is any doubt whether the average temperature can be used along with equation (19.4) to model the heat input to a batch reactor.

In all cases considered here, heat transfer was either considered to be absent (adiabatic operation) or the temperature was assumed to be uniform throughout the heat transfer fluid. In other words, in all cases considered here, $\dot{Q}$ is either equal to zero or it is given by equation (19.4). If the temperature is *not* uniform throughout the heat transfer fluid, equation (19.4) does not apply. Such situations will not be considered in this introductory course; a good heat transfer textbook and/or handbook should be consulted to find the appropriate expression for the heat transfer between the reaction volume and the heat transfer fluid along with correlations to determine the corresponding value of the heat transfer coefficient.

Once the appropriate set of design equations has been written and all negligible and zero-valued terms have been eliminated, it is necessary to solve those equations. The design equations will consist of a set of ordinary differential equations where each equation includes the derivative of only one dependent variable with respect to time. That is, it will be possible to write the design equations in the matrix form shown in equation (19.7) where the elements in the vector $\underline{y}$ may represent the number of moles of moles of a species, the temperature of the reaction volume or the temperature of the heat transfer fluid. In these equations, t is the independent variable, and it represents the elapsed time since the start of the processing step being modeled. As such, the value of the dependent variables, $\underline{y}$, will be known at $t = 0$. Thus, the design equations represent a set of initial value ordinary differential equations (ODEs). Except for a few very simple situations it will not be possible to solve these equations analytically, so here it is assumed that all solutions will be obtained numerically.

$$\frac{d\underline{y}}{dt} = \underline{f}\left(\underline{y},t\right); \quad \underline{y}\left(t = 0\right) = \underline{y}^0$$

(19.7)

There are many software packages that can be used to solve the design equations numerically, and you should use the one you feel most comfortable with. Supplemental Unit S5 presents a brief introduction to the numerical solution of initial value ODEs; if you aren't familiar with numerical solution of initial value ODEs, you should read Supplemental Unit S5. If you plan to use MATLAB to solve the design equations, Supplemental Unit S5 also presents template files that can be used to solve sets of initial value ODEs of the form given in equation (19.7). No matter what software package you use, when the

equations are written in the form of equation (19.7), you will need to provide three things as input to the software:

- the initial values of the dependent variables, that is, the values of each y_i at $t = 0$
- the final value of either t or one of the dependent variables
- code that evaluates each of the functions, f_i, given a value for t, values for each of the dependent variables, y_i, and any additional information given in the problem specification or found in handbooks and other reference sources

In addition to the dependent variables, y, and the independent variable, t, the functions, f_i, in the set of design equations are likely to contain constants as well as other quantities that vary during the processing step being modeled. The code that you provide to the ODE solver will need to calculate the values of such variables from the data given in the problem and the values of t and the dependent variables. For example, the mole balance design equations will contain rate expressions, and those rate expressions will contain rate coefficients and concentrations or partial pressures. The code you provide will need to calculate the values of these quantities in order to evaluate the functions, f_i. Equations (19.8) through (19.12) represent some of the more common equations used to calculate such quantities. Equation (19.12) is one of several possible forms of an equation to calculate heat capacity as a function of temperature; see Unit 2. The heat capacities appear directly in the energy balance, and they are also used to calculate the heat of reaction, which, in general, varies with temperature; again, see Unit 2.

$$k_j = k_{0,j} \exp\left\{\frac{-E_j}{RT}\right\} \tag{19.8}$$

$$C_i = \frac{n_i}{V} \tag{19.9}$$

$$P_i = \frac{n_i}{\sum\limits_{\substack{k = \text{all} \\ \text{species}}} n_k} P \tag{19.10}$$

$$P = \frac{RT \sum\limits_{\substack{k = \text{all} \\ \text{species}}} n_k}{V} \tag{19.11}$$

$$\hat{C}_{pi} = A_i + B_i T + C_i T^2 + D_i T^3 + \frac{E_i}{T^2} \tag{19.12}$$