

A First Course on Kinetics and Reaction Engineering

Unit 32. Ideal Semi-Batch Reactors

Overview

Unit 32 examines a way of augmenting the operating procedure for a batch reactor in order to enhance its performance characteristics under selected conditions. Specifically, this unit examines semi-batch reactors. In semi-batch processing, most of the reagents are treated as they would be under batch processing: they are put into the reactor prior to starting the reaction, and they are removed from the reactor after the reaction is terminated. In contrast to batch processing, during semi-batch processing, at least one reagent is added or removed while the reaction is taking place. This unit describes the modeling of reactors that are operated as semi-batch reactors.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- semi-batch operation

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:

- identify circumstances where semi-batch reactor operation might be advantageous
- formulate mole and energy balance design equations for a semi-batch reactor
- solve the semi-batch reactor design equations and use the results to perform a requested engineering task

Information

A semi-batch reactor is a batch reactor where one or more, but not all, of the reactants and products flows in or out during processing. Two illustrative examples are the neutralization of a batch of acid by the slow addition of a base (to control the rate at which heat is released) and esterification reactions where one of the products of the reaction boils off as reaction proceeds (and thereby allows the reversible reaction to proceed to high conversion). As one might expect, the design equations for a semi-batch reactor can be generated by modification of the batch reactor design equations.

The mole balance design equation starts with the batch reactor mole balance and *adds a variable, \dot{n}_i , to represent the net, instantaneous molar flow of species i into the reactor*, equation (32.1). This quantity may be a function of time; it is not necessarily a constant. For example, in semi-batch neutralization of an acid, the base may be added slowly at first and more rapidly as the neutralization proceeds. Similarly, the energy balance design equation starts with the batch reactor energy balance and then adds a term to account for the energy associated with the material flowing in or out. Specifically, energy enters or leaves the reactor with the flowing species as internal energy of the flowing molecules and as PV work that is done by the fluid in flowing in or out. In equation (32.2) these two forms of energy are combined in the form of the specific enthalpy of the species. As equation (32.3) shows for an ideal solution, this energy is equal to the energy required to heat or cool the material entering the reactor from

the stream temperature to the temperature within the reactor at the instant it is added, plus any latent heat if the material changes phase in going from the flow stream to the reactor. The discussion here has been worded as if the material enters because \dot{n}_i is defined as the net flow into the reactor. If the material actually flows out of the reactor, \dot{n}_i will be a negative quantity. Also, if material flows out of the reactor, it will most likely be at the same temperature as the reactor contents, but in a different phase.

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=all \\ \text{reactions}}} v_{i,j} r_j \quad (32.1)$$

$$\begin{aligned} \dot{Q} - \dot{W} = & \sum_{\substack{i=all \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,stream}) \\ & + \frac{dT}{dt} \sum_{\substack{i=all \\ \text{species}}} (n_i \hat{C}_{p,i}) + V \sum_{\substack{j=all \\ \text{reactions}}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt} \end{aligned} \quad (32.2)$$

$$\dot{n}_i (\hat{h}_i - \hat{h}_{i,stream}) = \dot{n}_i \left(\int_{T_{stream}}^T \hat{C}_{p,i} dT + \Delta H_{latent,i} \right) \quad (32.3)$$

If a species is leaving the reactor because it is boiling off, then the vapor composition is related to the liquid composition by thermodynamics. For example, if Raoult's law applies, then the vapor phase partial pressure of species i , P_i is equal to its liquid phase mole fraction, x_i , times its saturation vapor pressure, P_i^* , as given in equation (32.4). Of course, the partial pressures of all the species must sum to give the total pressure. Similarly, if Henry's law applies, then the liquid phase concentration and the vapor phase partial pressure are related as shown in equation (32.5), where h_i (no hat on the h) is the Henry's law constant for species i .

$$P_i = x_i P_i^* \quad (32.4)$$

$$P_i h_i = C_i \quad (32.5)$$

In fact, it is possible that there may not be a flow stream entering or leaving a semi-batch reactor while it is operating. Up to this point in this course, the reacting fluid in all reactors was a single phase (there may have been a solid phase catalyst in the reactor). Indeed, the batch reactor design equations are written assuming the reacting fluid to consist of a single phase. It has been noted in past units that when liquids are processed in a batch reactor, there is often some vapor phase head space above the liquid. In past units, when batch reactors were being evaluated, it has always been assumed that no reagents were transferred from the liquid phase into that head space. If, in fact, one reagent boils off from the liquid phase and accumulates in the head space, then the liquid phase is no longer operating as a batch reactor. Instead, the liquid phase must be modeled as a semi-batch reactor, even though there is no flow stream leaving the reactor. From the perspective of the liquid phase, that reagent is flowing out of the liquid phase.

Note also, that unlike a batch reactor, the fluid volume may not be constant in a semi-batch reactor. In the case where a liquid is present in the reactor, the fluid volume (which is where the reaction is taking place and which is the volume upon which the mole and energy balances are written) will typically change during processing. The fluid volume can be related to the moles of each species within the reactor. For example, if liquid mixture is ideal, the fluid volume can be found using equation (32.6), where M_i is the molecular weight and ρ_i is the pure component density of component i . Alternatively, if the system density is constant, the instantaneous volume of liquid in reactor can be related to the initial volume of liquid in the reactor and the volumetric flow into the reactor over time. In the case of a constant inlet volumetric flow rate, this relationship takes the form given in equation (32.7), where V^0 is the initial volume of liquid in the reactor and \dot{V} is the constant volumetric flow rate entering the reactor.

$$V(t) = \sum_{\substack{i=all \\ species}} \frac{n_i(t)M_i}{\rho_i} \quad (32.6)$$

$$V(t) = V^0 + \dot{V}t \quad (32.7)$$

If a gas was being fed into a closed vessel, then the fluid volume would be constant, but the pressure would vary with time. The derivative of the pressure with respect to time in equation (32.2) would then be re-expressed in terms of the moles and the temperature using an appropriate equation of state such as the ideal gas law.

The semi-batch reactor design equations are ordinary differential equations, and they are solved in the same manner as the batch reactor design equations. A mole balance is written for every reactant and product along with an energy balance, and the resulting set of ordinary differential equations is solved numerically. To do so, the initial values of the independent and dependent variables must be specified along with the final value of either the independent variable or one of the dependent variables. In addition, code must be provided that is given values for the independent and dependent variables and that uses them to evaluate the differential equations being solved (see Supplemental Unit S-5).