A First Course on Kinetics and Reaction Engineering
Unit 37. Overview of Multi-Phase Reactors

Overview

Unit 37 presents an introduction to the modeling of reactors containing two-phases. In Part III of the course, packed bed tubular reactors and semi-batch reactors were the only systems considered that involved two phases. For packed bed reactors assumptions were made that allowed the design equations to be formulated as if the solid phase was not even present. Often, the assumptions that allowed that simplification are not valid and it becomes necessary to explicitly account for the presence of two phases. This was done in the case of a semi-batch reactor where one product evaporated from the liquid phase, but again using some assumptions (no concentration or temperature gradients in either phase) that will not always be valid. This unit shows that to properly model such systems, it is necessary to write design equations separately for each phase. It is additionally necessary to model the exchange of material and energy between the two phases in that model, which will be considered in Section B of Part IV. This unit concludes with a brief overview of different kinds of process equipment for multi-phase reactions.

Learning Objectives

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

- fluidized bed reactor
- riser reactor
- trickle bed reactor
- slurry reactor
- spray tower reactor
- bubble column reactor
- laminar flow reactor
- reactive distillation
- membrane reactor

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 that the modeling of multi-phase reactors typically requires design equations for each phase present in the system.

Information

To this point in this course we have only considered two situations involving reactors wherein two phases were present and involved in reaction. One of these was the case of a tubular packed bed reactor. In that case we made a number of assumptions, some of questionable validity, with the end result being that we treated the reactor as if the solid catalyst packing wasn't even there. Unit 12 described some experimental and computational tests that can be used to determine whether those assumptions are valid for a laboratory reactor. Unit 38 will examine situations where those assumptions are not valid,

and consequently where the PFR model cannot be used in the simple manner we have employed up to this point.

The other situation where we have considered a reactor with two phases present and participating in the reaction was the case of a semi-batch reactor. Specifically, Example 32.2 involved the modeling of a semi-batch reactor wherein one of the products formed in the liquid phase evaporated into the vapor phase headspace in the reactor. In that example, the reaction was reversible, and the evaporation of one product from the liquid phase resulted in a higher reactant conversion than would be observed if the reaction was restricted to only the liquid phase. In that example we again made an assumption (that the liquid and vapor phases were always in thermodynamic equilibrium) that simplified the analysis of the reactor.

In the semi-batch reactor example of Unit 32, it was necessary to write two sets of mole balances, one for the liquid phase and a second set for the vapor phase. In general, when reactors contain multiple phases it is necessary to write a set of mole and energy balances for each phase that is present. In addition, it is usually also necessary to develop models for the rate of exchange of each species between each pair of phases present. We avoided that in the semi-batch reactor analysis of Unit 32 by assuming phase equilibrium. Units 38 through 40 describe a few ways to model the rate of mass transfer between phases for heterogeneous catalytic reactions, gas-liquid reactions and gas-solid reactions. We will see that most often there are concentration and temperature gradients in the vicinity of the phase interface. As a result, the rates of mass and heat transfer are often described in terms of heat and mass transfer coefficients and models for diffusion due to the concentration gradients that are present.

In some cases, the reactors used for two phase reactions are very similar to the ideal reactors that were used in Parts II and III of the course. That is, a simple stirred tank or tubular packed bed reactor can be used in some situations, with the necessary difference of modeling each of the phases present. For a packed bed, the mole and energy balances on the flowing fluid phase are the very similar to the PFR model. For stirred tank reactors containing two phases, there are some additional factors that must be taken into consideration.

In a stirred tank reactor containing an agitated, two-phase, reacting mixture, one of the two phases will typically be continuous while the other phase is dispersed (e. g. as bubbles of droplets within the continuous phase). It is reasonable to expect the bulk of the continuous phase to be well-mixed. However, the dispersed phase may or may not be well-mixed depending upon how the agitation system is designed. Heat transfer may also be complicated; it could involve heat transfer from a coil or jacket to each of the two phases as well as heat transfer between the two phases. In short, it isn't possible to write a single set of design equations for all two-phase stirred tank reactors. Each reactor must be considered individually, and appropriate mole and energy balances must be written for each of the phases present. In almost all cases it will also be necessary to model the transfer between phases in ways similar to those discussed in Units 38 through 40.

In other cases, a multi-phase reactor may not closely resemble a stirred tank or tubular reactor. The modeling of such reactors will not be considered here, but a few examples are briefly described in the following paragraphs.

Fluidized Bed Reactors. Fluidized bed reactors are vessels that contain relatively fine grains of solid catalyst. Gas enters the bottom of the vessel, usually through some sort of distributor plate that serves to spread the gas flow across the cross-section of the reactor vessel. The gas velocity is large enough to cause the solid grains to fluidize. That is, the particles move about with an appearance similar to an agitated liquid. Fluidized beds are sometimes used in the catalytic cracking of heavier hydrocarbons in a refinery.

Riser Reactors or Entrained Flow Reactors. Riser reactors are similar to fluidized bed reactors except that the gas velocity is larger. As a consequence, the fine solid particles become entrained in the gas flow and are carried up and out of the reactor by the flowing gas. The solids are then separated from the product gas and recycled back to the reactor. Riser reactors permit some very elegant engineering of catalytic cracking processes. In that case, the entrained catalyst particles rapidly deactivate due to the deposition of carbon on and in the particles. After they have been separated from the products, the catalyst particles are returned to a second reactor bed wherein the deposited carbon is burned off. This generates heat which raises the temperature of the catalyst particles. By the time they return again to the riser reactor they are sufficiently hot to provide most or all of the heat needed to sustain the endothermic cracking reaction in the riser.

Trickle Bed Reactors. Trickle bed reactor involve three phases. Solid catalyst particles form a catalyst bed as in some of the reactors studied in earlier units. In a trickle bed reactor, liquid typically flows down through the packed bed at a relatively low flow rate. It is often preferred that the liquid coats the surfaces of the particles making up the bed, but that it does not fill the void spaces between the particles. A gas then flows upward through those spaces. Trickle beds are used when a solid-catalyzed reaction involves one liquid phase reactant and a second gas phase reactant. Trickle bed reactors are used commercially in hydrodesulfurization reactors. In hydrodesulfurization reactors, a hydrocarbon feedstock containing sulfur (as thiophenes and other organo-sulfur hydrocarbons found in crude oil) is treated with hydrogen in order to remove the sulfur in the form of H_2S.

Slurry Reactors. Slurry reactors offer another way to conduct solid catalyzed reactions that involve reagents from both the liquid phase and the gas phase. In a slurry reactor, the solid catalyst particles are suspended in the continuous liquid phase, forming a slurry. The gas phase reactants then bubble through the liquid phase slurry. Slurry reactors can be used in the hydrogenation of oils and in the production of waxes via reaction between carbon monoxide and hydrogen.

Spray Tower Reactors. Spray tower reactors are vessels where a liquid enters at the top of the vessel in the form of a spray of very small droplets. A gas enters the reactor from the bottom and flows up through the spray. As such, spray towers are used for gas-liquid reactions. They are particularly useful when the gas phase reactant is only sparingly soluble in the liquid or when the diffusion of the gas into the liquid is relatively slow. By producing the liquid as a spray of fine particles, the interfacial area (per mass of liquid) is high and the diffusion path length for the gas is small because the droplets are small.

Bubble Column Reactors. Bubble column reactors are an alternative way to conduct gas-liquid reactions. In a bubble column reactor the liquid phase is continuous over the entire cross section of the

column. The liquid may flow either upward or downward. The gas reactant then enters at the bottom of the column and rises through it in the form of bubbles rising through the liquid phase.

Reactive Distillation. There are situations where using a distillation column as a chemical reactor can offer significant advantages. Usually distillation columns are used to separate mixtures on the basis of their volatility. If a reaction is equilibrium limited, removal of a product via distillation allows the system to reach a greater conversion than would occur without the simultaneous separation. Similarly, separation of products while they are reacting can affect the selectivity of a reaction network.

Membrane Reactors. Membrane reactors also have the potential to combine reaction and separation in a single vessel. Typically one wall of a membrane reactor is permeable to one or more of the reagents involved in the reaction. As such, it allows the selective removal of the permeable component(s) from the reaction mixture. This can have the same advantages for conversion and selectivity as described above for reactive distillation. Membrane reactors are not in common use in commercial processes at the time of this writing.

Laminar Flow Reactors. When the Reynolds number of a fluid flowing in a tubular reactor is less than ca. 2100, plug flow will not occur. Instead, a parabolic velocity profile develops where the axial flow velocity is zero right at the wall and reaches a maximum at the centerline of the tube. One can perform mole balances on a differential ring of fluid (differentially thick in both the axial and radial directions) much the same as was done in developing the PFR design equations. Taking the limit as the differential dimensions approach zero leads to a set of differential equations that constitute the design equations under conditions of laminar flow. If the viscosity and other fluid properties depend strongly upon concentration or temperature, the resulting equations can become quite complicated. Note: laminar flow reactors usually contain a single fluid phase, but they have been included in this unit simply because, like the multi-phase reactors listed above, they require design equations that differ from the ideal CSTR and PFR models used throughout this course.