A First Course on Kinetics and Reaction Engineering
Unit 25. Reaction Engineering of PFRs

Overview

Unit 25 begins the analysis of the third and final ideal reactor type, namely the plug flow reactor. This unit describes the kinds of tasks one may need to accomplish during the reaction engineering of PFRs. The information is very similar to that for CSTRs, since both are flow reactors. It also includes a discussion of the qualitative analysis of PFRs, showing that their performance is often the same as a batch reactor if one substitutes the PFR residence time in place of the duration of a batch reaction process.

Learning Objectives

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:

- List situations where the use of a PFR is advantageous and situations where it is disadvantageous and link those situations to distinguishing features of PFRs.
- Predict how (qualitatively) composition and temperature will vary during the course of a specified single reaction taking place in an isothermal or adiabatic steady state PFR.
- Analyze (qualitatively) the effect a change in the mode of operation of a steady state PFR upon its concentration and temperature as a function of space time.

Information

This unit considers the reaction engineering of plug flow reactors; it complements Units 18 and 21, which considered reaction engineering of batch reactors and CSTRs, respectively. One significant difference between a PFR and these other reactor types is that the environmental variables can vary both spatially and temporally. In batch reactors and CSTRs there was no spatial variation due to the assumption of perfect mixing. In a *steady state* PFR, the composition and temperature at any one position along its length will be constant; at a different position along its length, the composition and temperature will again be constant, but they will be different than they were at the first position. If the PFR is not at steady state, then the composition and temperature will be changing over time when observed at a fixed point along the length of the reactor.

As with the CSTR, a PFR is usually designed to operate at steady state, but it there will be times when it undergoes transient operation. For example, transients occur when the reactor is first started-up, when it is shut down, when an operating parameter such as a feed rate or feed temperature is deliberately changed, or when such a parameter changes unexpectedly. We've already seen that the PFR design equations governing steady state operation are ordinary differential equations. When the reactor is not at steady state, the design equations take the form of partial differential equations.

The reaction engineering of PFRs is like that of the other reactor types. An accurate mathematical model of the reactor is developed and used to perform some engineering task. Once again, the task can

be either a design task, where the goal is to specify the size and operating parameters for the reactor, or an engineering task where the specifications are known and the task involves some aspect of the reactor's operation. The ultimate goal remains one of maximizing the rate of profit from the system as a whole (not just the reactor), and consequently the reaction engineering task becomes a problem in constrained optimization. That is, the rest of the system often imposes limitations or restrictions on how the reactor can be operated, and the engineering task is to maximize system profits within the imposed limits.

In this course, the economics of the overall process will not be used, but as a general rules of thumb it is desirable to operate at the highest conversion and flow rate possible, using the smallest volume possible and the least amount of external heating or cooling while maximizing selectivity for the desired product. In most cases, these goals cannot all be satisfied, so the reaction engineer seeks to achieve the best compromise between them.

Just as the CSTR had certain characteristics that made it particularly appropriate in certain circumstances, the PFR also has some distinguishing features that can be used to advantage. Since no agitation is involved in a PFR, it is equally well suited to either gases or liquids. If the reaction requires the use of a solid catalyst, a PFR is preferred over a CSTR. This is so because it is nearly impossible to stir a solid-gas mixture, and while a solid-liquid mixture can be stirred, doing so often causes damage to the catalyst and to the agitator due to abrasion. In a PFR, the temporal variations observed in a batch reactor become spatial variations; that is, the concentration will vary continually along the length of the reactor with the highest reactant concentration at the inlet and lower reactant concentrations as one progresses along the reactor.

Heat transfer is another feature that differs significantly between the two types of continuous flow reactors, namely CSTRs and PFRs. Recall, in a CSTR, one can use a jacket around the reactor, but if additional heat transfer area is required, a coil can be submerged within the fluid. In this way, the ratio of reactor volume to heat transfer area can be made to span a fairly wide range of values. With a PFR it is not possible to add a heating/cooling coil within the fluid volume. All the heat transfer takes place through the wall of the reactor. Consequently, the only way to vary the ratio of heat transfer area to fluid volume is by using reactors of different diameter. Unfortunately, as one goes to smaller and smaller tube diameters, the pressure drop through the reactor becomes larger and larger. This imposes a practical lower limit upon the reactor diameter and thereby an upper limit on the ratio of heat transfer area to fluid volume than can be attained in a PFR. In some cases, engineers can get around this limitation by breaking the plug flow reactor into several segments and either installing a heat exchanger between the segments or (for cooling) by injecting cold feed into the process between the stages. These systems are easy to analyze because each segment still behaves as a single PFR.

Generally, continuous flow reactors are preferred over batch reactors when very large quantities of the product are needed. On the basis of its distinguishing features, a PFR is particularly well suited to situations involving gases and where the heat transfer demands are not excessive. The spatial variation of the composition and temperature along the length of the reactor give it advantages when the reaction

rate or selectivity is favored by higher reactant concentrations and by temperatures near the feed temperature.

In a steady state CSTR the composition does not vary temporally or spatially while in a batch reactor, it varies temporally, but not spatially. In a *steady state PFR* the composition varies spatially, but not temporally. We saw in Unit 21 that in order to qualitatively analyze the performance of a CSTR, it was necessary to consider how the performance varied as the space time changed. Then, in order to compare batch reactors and CSTRs, it was necessary to assess how the composition varied during the time the fluid was reacting. In this case there was again a difference: as the fluid reacts in a batch reactor, the composition changes continually but in a CSTR, the fluid immediately jumps to the final composition which then does not vary as reaction proceeds.

In order to qualitatively analyze a PFR, it is again necessary to consider how the performance varies as the space time changes. Recall the derivation of the PFR design equations in Unit 17. The mole balance was performed on a differentially thick fluid element like that shown in Figure 25.1. The fluid element is perfectly mixed in the radial direction, and it is only differentially thick in the axial direction. Thus, the fluid within the differential element is perfectly mixed, and it does not mix with any of the other fluid in the reactor. In essence, it is a small batch reactor that moves through the tube. Reaction can take place in this little differential batch reactor for as long as the fluid element is within the tubular reactor. Thus, a differential fluid element flowing through a plug flow reactor is like a tiny batch reactor with a processing time equal to the plug flow reactor space time.

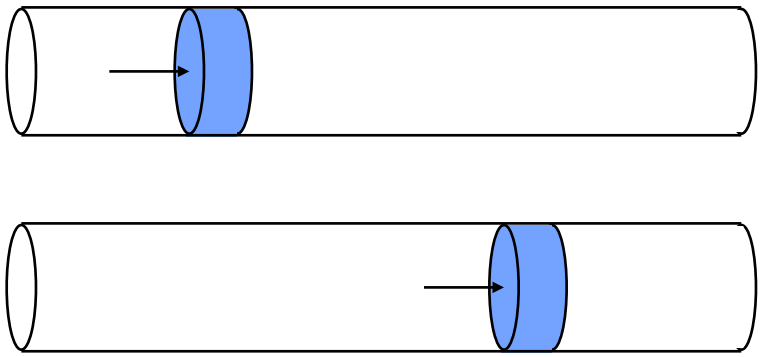

Figure 25.1 Differential fluid element progressing through the tubular reactor.

This makes it very easy to qualitatively analyze the performance of a PFR. The variation of concentration, conversion, temperature, rate, etc. as a function of space time in a PFR is equal to that in a batch reactor as a function of processing time. When the fluid element first enters the reactor, the reactant concentration is at its greatest, and it decreases steadily as the reaction takes place (that is, as the fluid element flows through the plug flow reactor). Since we already know how to qualitatively analyze a batch reactor and how to compare it to a CSTR, then we also know how to qualitatively analyze a plug flow reactor and compare it to a CSTR: simply replace the batch processing time with the plug flow reactor space time.

For purposes of qualitative analysis, it is acceptable to treat a fluid element in a plug flow reactor as equivalent to a differential batch reactor. However it is important to be aware that there are some subtle differences. Most batch reactors used in chemical processing have a constant volume. This is not necessarily so for a plug flow reactor. For example, if the fluid is an ideal gas and the temperature is increasing as the fluid passes through the reactor, then the differential fluid element will be expanding as it moves through the reactor. One might be tempted to account for this effect by equating the differential fluid element to a constant pressure batch reactor instead of a constant volume batch reactor. Unfortunately, this would not be correct either. In a plug flow reactor, the pressure will drop as the fluid flows through the reactor due to the friction between the fluid element and the reactor wall. Recall that the plug flow reactor has an additional design equation to account for this process.

Thus, while it is acceptable to treat a fluid element within a plug flow reactor as a small batch reactor in order to qualitatively assess its performance, this approach should not be used when performing a quantitative analysis. In that case one should write and solve the plug flow reactor design equations. There is another difference, as well. With a batch reactor there can be a processing “recipe” where the operating parameters can be changed from one step in the recipe to the next. In a steady state plug flow reactor, the corresponding “recipe” is only a single step because the operating parameters are constant.