A First Course on Kinetics and Reaction Engineering
Unit 21. Reaction Engineering of CSTRs

Overview

Unit 21 is the first of four units that examine the reaction engineering of CSTRs. The topics covered in this unit are analogous to those in Unit 18 except they apply to CSTRs instead of batch reactors. Specifically, Unit 21 considers typical reaction engineering tasks that involve CSTRs. It also shows how to perform a qualitative analysis of a CSTR, building upon and extending the intuitive "feel" for how reactors behave that was initiated in Unit 18. It also differentiates steady state operation from transient operation.

Learning Objectives

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

- steady-state operation
- transient operation

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

- space time

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 factors that might favor the selection of a CSTR over other reactor types.
- List disadvantages of CSTRs compared to other reactor types.
- Compare and contrast the temporal and spatial variation of the environmental variables during the use of a CSTR to the temporal and spatial variation of the environmental variables during the use of other types of reactors.
- Predict and explain, on physical grounds without using any equations, why composition and temperature vary with space time as they do when one or more reactions take place in a CSTR being operated in a known and specified manner.
- Select preferred modes of operation of a CSTR for a specified reaction without writing or solving any equations.
- Qualitatively compare the behavior of a CSTR to that of a perfectly mixed batch reactor for a specified reaction and mode of reactor operation.

Information

In the present unit and the one to follow, the focus will be upon *steady-state operation* of CSTRs. The term steady-state refers to the situation where there are no temporal variations of any of the variables of the system. The inlet flow rate of each component is constant over time, the inlet temperature and pressure are constant over time, the volume of fluid in the reactor is constant over time, the temperature, pressure, and composition of the fluid within the reactor are each constant over time, the outlet flow rate of each component is constant over time, etc. CSTRs are usually designed to operate at steady-state for extended periods of time. Most commonly, processes involving CSTRs are designed on

the basis of their steady-state performance. That is, the goal of the reaction engineer is usually to maximize the rate at which the overall process makes profit under the assumption that it will spend most of its time operating at steady-state.

In order to get a reactor process operating at steady-state, it must first go through a period of *transient operation* known as start-up. Start-up is not the only type of transient operation; any time one or more of the system's variables undergoes a temporal variation, the system is undergoing transient operation. For example, if you begin with an empty reactor and set the inlet flows of each component, the volume and/or composition of the fluid within the reactor will be changing as the reactor fills. Thus, this is a form of transient operation. Any time an adjustment is made to a system at steady state, there will typically be a period of transient operation until (in most cases) the system re-establishes a new steady-state. The key to recognizing transient operation is to remember that it involves a change in one or more variables over time. Transient operation will be considered in Unit 23.

As was the case for batch reactors, reaction engineering of CSTRs involves creating a mathematical model for the reactor system and then using that model to perform some type of engineering analysis. Once again it is possible to arbitrarily distinguish reactor design from other types of engineering analyses. Recall that the objective of reactor design is to specify the reactor system whereas in other engineering analyses the reactor system is already established. As was the case with the batch reactor, the objective of reactor design is to specify a reactor system that will maximize the rate of profit of the process that incorporates it, while ensuring the safety of plant employees and the general public and complying with all applicable laws and regulations. In the absence of economic data, the following general guidelines will typically lead to a rate of profit that is close to the optimum.

- reactor productivity should be as high as possible (high conversion and high flow rate)
- reaction volume should be as small as possible
- the heating or cooling demand should be as small as possible (or it should be well-integrated with other parts of the overall process so that external heating and cooling demands of the overall process are minimized)
- the selectivity should be has large as possible

It won't usually be possible to satisfy all these guidelines; some will be determined by the specifications of the problem or assignment, and the best compromise is then made among the rest.

Reactor design involves specifying the reactor system and how it is operated. For a CSTR this typically includes specifying the reaction volume, the heat transfer area within the reactor, the steady-state flow rates of each component into the reactor, the inlet temperature and pressure of each component entering the reactor, and the flow rate and temperature of the heat transfer fluid. It also includes specifying the procedure that should be followed to start up and to shut down the reactor. In certain cases, to be discussed in later units, the steady state that is reached depends upon the manner in which the reactor is started. Similarly, in some cases using the wrong sequence of steps when shutting down a reactor can lead to a dangerous condition (like an explosion).

If an engineer is assigned the task of designing a reactor for a new installation, one of the first questions that will arise is that of what type of reactor to use. Each reactor type has its own unique and

distinguishing features which lead to certain advantages and disadvantages associated with its use. For example, batch reactors have the advantage of being very flexible, but have the disadvantage of being labor intensive. A CSTR, in contrast to a batch reactor, operates continuously. As such, CSTRs are well suited to making very large quantities of product. Other distinguishing features of a <u>steady-state</u> CSTR include the following.

- Within the reactor, the environmental variables do not change either spatially or temporally. The reaction takes place at a single temperature, pressure and composition that corresponds to the final outlet conditions.
  - This usually means that the reaction takes place at high product concentration and low reactant concentration.
- Because heating or cooling can be effected via a coil of heat transfer tubing submerged within the reacting fluid, there is some flexibility in the amount of heat transfer that can be accomplished per volume of reacting fluid.
- While some more complicated reactors can be modeled as CSTRs, a stirred tank is generally more amenable to a liquid phase system than to gases because it is hard to "stir" gases. (The recirculation type CSTRs that were described for laboratory use in kinetics studies often are not practical at a commercial scale.)

The distinguishing features listed above result in CSTRs being particularly well-suited for use with exothermic liquid phase reactions, auto-catalytic reactions, reactant inhibited reactions and auto-thermal reactions. For a "normal" reaction that is not highly exothermic, other reactor types may be better. The reason for this is that the reaction takes place at the final outlet temperature, pressure and composition. That is, the reaction takes place at low reactant concentration and high product concentration. Normally the rate of reaction decreases as the reactant concentration decreases and as the product concentration increases. Consequently, in a CSTR, the rate throughout the entire reactor volume will be low. Thus, for "normal" reactions, a reactor that keeps the reactant concentration higher initially, such as the batch reactor (or the PFR that will be discussed in the next section of the course), will make better use of the reaction volume than a CSTR.

The ability to write and solve reactor design equations, by itself, is not sufficient to make one a good reaction engineer. Among other skills and abilities, one additionally needs to have a physical appreciation for how reactive processes occur and an intuitive sense for how a reactor will respond to a given change in the way it's being operated. The remainder of this unit attempts to help build that physical understanding from which an intuitive feel will eventually emerge for systems involving steady state CSTRs. This is done by describing the qualitative analysis of a CSTR in much the same way that Unit 18 described the qualitative analysis of a batch reactor.

The qualitative analysis of a steady state CSTR is fundamentally different from the qualitative analysis of a batch reactor. Recall that the qualitative analysis of a batch reactor was based upon how the composition and temperature would change during the first few small intervals of time. In a steady state CSTR, the composition and temperature do not change over time, so clearly that approach cannot be

used. Instead, the qualitative analysis of a CSTR considers how the outlet composition and temperature will change as the average residence time, or space time, changes. Recall from Unit 13 that the space time for a flow reactor, including a CSTR, is defined as shown in equation (21.1). The space time is a measure of the average length of time that the reacting fluid spends within the reactor. That is, the space time is a measure of how long the reagents are allowed to react.

$$\tau = \frac{V}{\dot{V}^0} \tag{21.1}$$

If the space time is a measure of how long the reagents are allowed to react, then the variation of the outlet composition and temperature of a CSTR as a function of space time is expected to be similar to the variation of those quantities with processing time in a batch reactor. As an example, consider a typical reaction taking place isothermally in a CSTR. At very small space times, there isn't much time for reaction to occur, so conversion is small. As a consequence, the reactant concentration is high and, for a typical reaction, the rate is high. At longer space times, there is more time for the reaction to occur, and consequently the conversion is greater. The greater concentration means that the reactant concentration is smaller, and consequently, for a typical reaction, the rate is smaller. This trend of increasing conversion, decreasing reactant concentration and decreasing rate of reaction with increasing space time means that a plot of conversion versus space time would start at zero when the space time was equal to zero. Its initial slope would be positive and it would be concave downward since the rate is decreasing as the space time increases. This trend will continue until eventually, the rate goes to zero due to either the complete consumption of all reactant (for an irreversible reaction) or due to the attainment of thermodynamic equilibrium. Figure 21.1 shows this behavior, f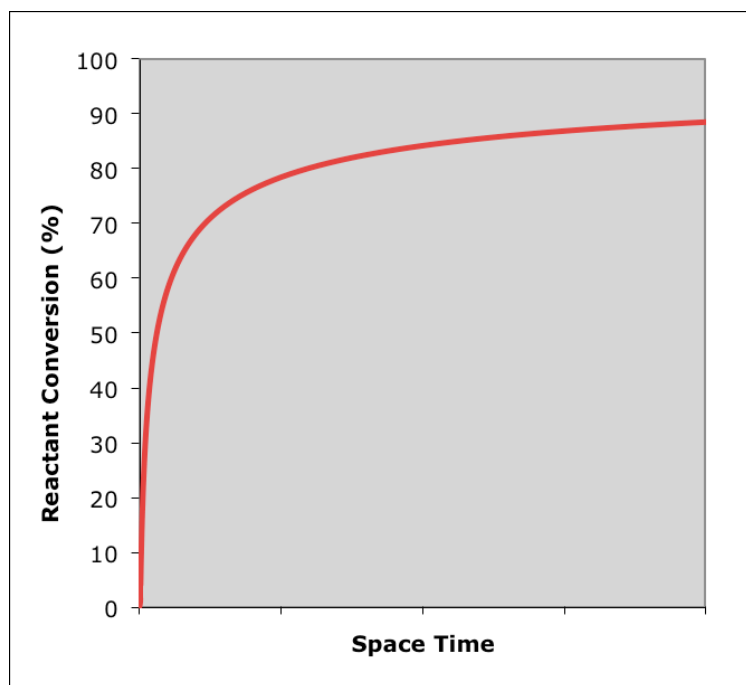or a typical reaction, but it does not extend to sufficiently large space times for the rate to have reached zero. That is, in Figure 21.1, the conversion is still increasing at the highest space time shown; the curve has not yet become horizontal. A plot of reactant concentration versus space time would start with the concentration being equal to the feed concentration at a space time of zero. It would have a steep negative slope initially, with the steepness of the slope decreasing continually until it eventually became equal to zero. That is, the curve would be concave upward. A plot of the reaction rate versus space time would have its greatest value at a space time

Figure 21.1 Reactant conversion versus CSTR space time for an irreversible reaction taking place isothermally.

of zero, and, for a typical reaction, it would decrease monotonically with increasing space time.

If you compare the variations just described for CSTRs as a function of space time to the variation of conversion, reactant concentration and reaction rate versus reaction time in a batch reactor, you will see that the behavior is very, very similar. Temperature variations with space time for CSTRs are also found to be very, very similar to temperature variations with reaction time for batch reactors. Thus, to qualitatively analyze the performance of a CSTR, one can use a batch reactor qualitative analysis, substituting the space time for the reaction time.

While the shape of a CSTR conversion versus space time plot is very similar to the shape of a batch reactor conversion versus reaction time plot, the two will not be identical. This can be seen in Figure 21.2 where the batch reactor conversion versus reaction time has been added to the CSTR conversion versus space time from Figure 21.1. It is very important to understand the reason why the two curves are not identical, and once again, a qualitative comparison will provide the necessary insight. The key aspect of the analysis is to compare how the concentration varies during the time that reaction is taking place.

Figure 21.2 Comparison of batch and CSTR conversion as a function of space time.

We already know that the concentration of reactant in a batch reactor will be the largest at the start of the reaction and it will decrease over time as the reaction takes place. As a consequence, for a typical isothermal reaction, the rate will initially be larger and will decrease over time as the reaction takes place. This is fundamentally different from a CSTR. As soon as fluid enters a CSTR, it is immediately mixed with the entire contents of the reactor so that its concentration immediately equals the final, outlet concentration. For the entire time it spends within the CSTR, its concentration will be constant at this value. As a consequence, the rate of reaction will be low and constant for the entire time that reaction occurs.

Now consider the situation where the initial composition in a batch reactor is equal to the composition of the feed to a CSTR. Suppose the two reactors are operated with the CSTR space time equal to the batch reactor processing time. Under such circumstances, amount of time that the fluid in each of the two reactors is allowed to react will be equal. For that whole period of time, the fluid in the CSTR will be reacting at a low rate, corresponding to the outlet composition from the reactor. In contrast, the initial rate in the batch reactor will be greater than the rate in the CSTR, but it will decrease continually
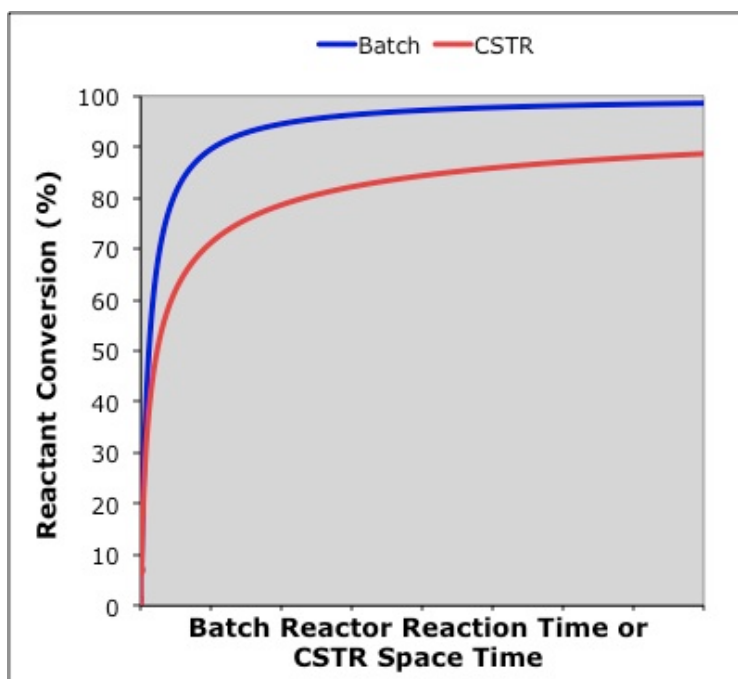
as the reaction proceeds. Since the fluid in the batch reactor is reacting at a higher rate, it will take less than the full processing time for the reactant concentration in the batch reactor to fall to the point where it equals the reactant concentration in the CSTR. Of course, the fluid in the batch reactor will continue to react for the entire processing time, so the end result is that the conversion in the batch reactor will be greater than the conversion in the CSTR when the batch processing time and the space time are equal. That is why the batch reactor conversion profile in blue in Figure 21.2 is always above the (red) CSTR conversion profile.

It may be useful to summarize for the situation where (a) the initial/feed compositions are equal and (b) the processing/space times are equal. In the CSTR, the fluid is allowed to react for a period of time equal to the space time, and during that period of time the rate and the concentration of reactant are constant. In the batch reactor, the fluid is also allowed to react for a period of time equal to the CSTR space time. At the start of that period of time, the reactant concentration and the rate of reaction are larger than in the CSTR. By the end of that period of time, the reactant concentration and the reaction rate are smaller than in the CSTR. This can be seen in Figure 21.3. Since the final concentration of reactant is smaller in the batch reactor, and the reactors had equal initial/feed concentrations, the conversion in the batch reactor is greater. Conversely, if the conversions in the two reactors are equal, then the batch reactor processing time will be smaller than the CSTR space time.

Thus, the differences in behavior shown in Figure 21.2 for an isothermal reactor, can be attributed to the difference in the reactant concentration as a function of the time spent in that isothermal reactor, as shown in Figure 21.3. If the reactor is not isothermal, then there will also be differences in the temperature as a function of time spent in the reactor. In order to start to understand the consequences of these differences, let's consider an irreversible reaction that is being run adiabatically. The difference between the two reactors will now be related to differences in both the reactant concentration and the temperature over the time period that the reaction is occurring.

We already know that in a batch reactor, the temperature will increase monotonically as the time a fluid element stays in the reactor increases. We also know that as a consequence, the rate will increase as a function of time spent in the reactor up to some critical conversion. Up to that point
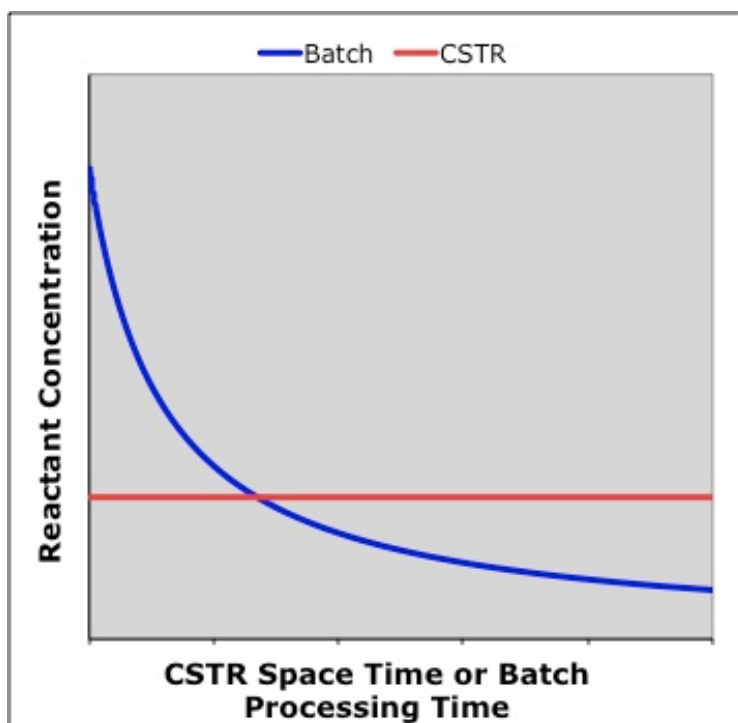

Figure 21.3 Reactant concentration during the time that the reaction is taking place in a batch reactor and a CSTR.

increasing temperature is predominating over the decreasing reactant concentration. At the critical conversion, the rate will reach a maximum and for the remainder of the time spent in the reactor, the rate will decrease because the effect of decreasing reactant concentration is predominating over the increasing temperature. (If you didn't know this, go back and review Unit 18 paying particular attention to Figure 18.5 and the discussion associated with it.) In contrast, as soon as the fluid enters a CSTR, it is immediately heated to the final outlet temperature, and the temperature stays constant at this value for the entire time the reaction takes place. Additionally, as noted earlier for the isothermal case, the reactant concentration remains low and constant for the entire time the reaction takes place.

Thus, at the start of the batch reaction, the reactant concentration will be higher than that in the CSTR while the temperature will be lower. So which of these effects will predominate? It depends, of course on how strongly the reaction rate depends upon temperature (i. e. the magnitude of the activation energy) compared to how strongly it depends upon reactant concentration (i. e. the reaction order). For given reaction kinetics (activation energy and order), there will be a critical conversion. If the CSTR operates at a space time where the overall conversion is less than the critical conversion, then the rate in the batch reactor will be less than the rate in the CSTR (the temperature effect will predominate). Above the critical conversion, the opposite will be true.

Figure 21.4 compares typical behavior for an adiabatic batch reactor, an adiabatic CSTR and an isothermal CSTR. It can be seen that at low space times, conversion in the adiabatic CSTR is greater than in the adiabatic batch reactor. In this region, the temperature effect is predominating. While the CSTR conversion is greater than the batch conversion, it is still less than the critical conversion just mentioned. The critical conversion is the point where the two adiabatic reactor conversion profiles cross. At higher space times, i. e. above the critical concentration the conversion in the batch reactor is greater because the concentration effect predominates.

We've noted before that generally, temperature has a greater effect than concentration, and this can be seen in Figure 21.4 when the adiabatic CSTR is compared to an isothermal CSTR. If the space time scale is expanded, as in Figure 21.5, this becomes even more apparent. Clearly, *for an exothermic reaction, adiabatic operation of a CSTR has*
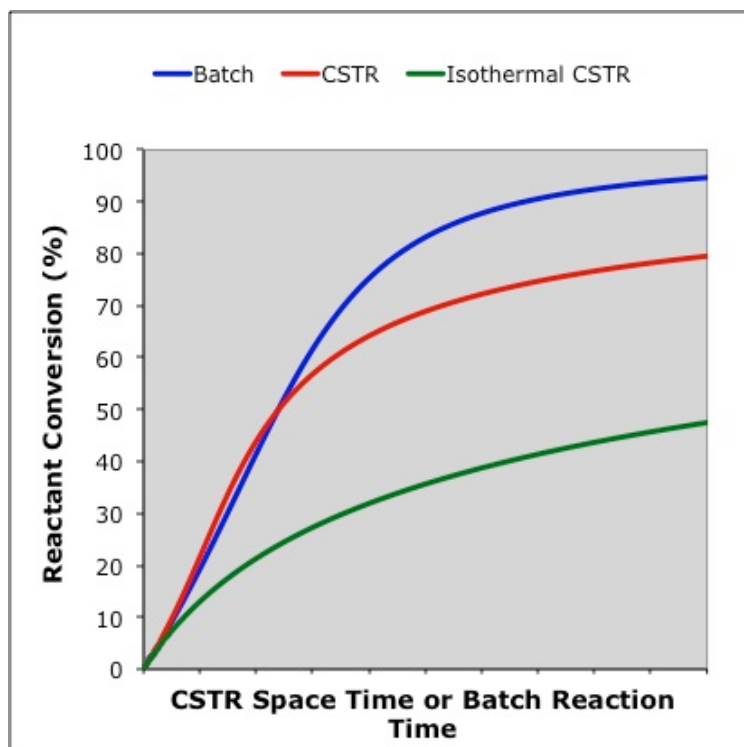

Figure 21.4 Comparison (at lower space times) of reactant conversion versus space time for an adiabatic batch reactor, an adiabatic CSTR and an isothermal CSTR.

significant benefits compared to isothermal operation.

Qualitative analyses of the type just presented can be useful when troubleshooting a CSTR system. They are also helpful at the earliest stages of reactor design, specifically at the point where a decision must be made as to what type of reactor to use and how that reactor should be operated (heated, cooled, adiabatic). Of course, quantitative analysis should must still be performed, as illustrated in the preceding qualitative analysis of adiabatic reactors. In a qualitative analysis, for example, there is no way of knowing the value of the critical conversion (or equivalently, the space/ processing time) where the conversion profiles cross in Figure 21.4.
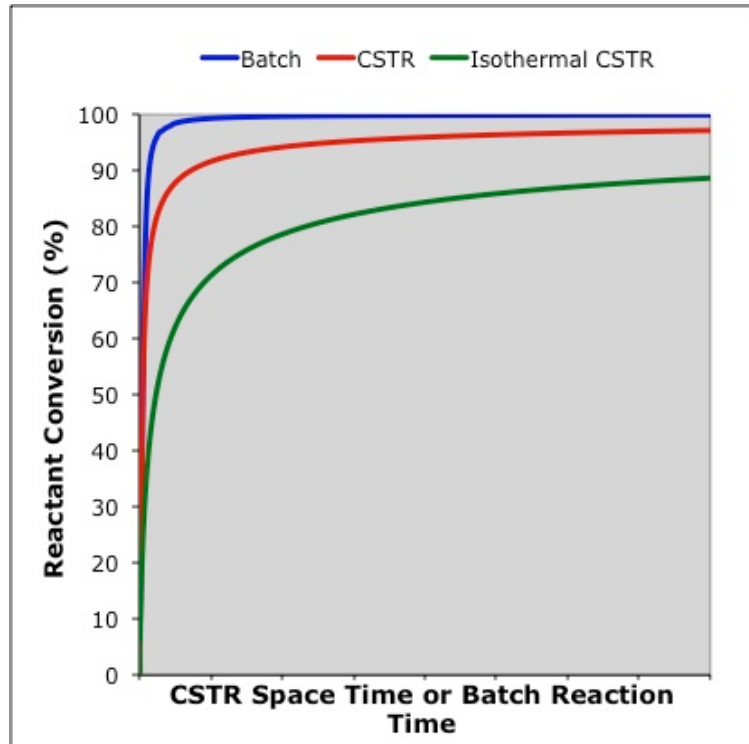

Figure 21.5 Comparison (at higher space times) of reactant conversion versus space time for an adiabatic batch reactor,