A First Course on Kinetics and Reaction Engineering
Unit 23. Analysis of Transient CSTRs

Overview

When designing a continuous process, it is often assumed that the system will operate most of the time at steady state. Nonetheless, analysis of transient behavior is an essential and critical part of the overall design of a system. In the case of CSTRs, transient analysis is used to determine the best way to start up the reactor and to shut it down. It is used to understand how the reactor system will respond to changes in its operating parameters, be they intentional or unexpected. Another use of transient analysis is in the design of control systems for the reactor system. This unit describes setting up the transient CSTR design equations for a system, common simplifications of those equations, and a general approach to solving them for common transient CSTR engineering purposes.

Learning Objectives

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

- operating parameter
- system response
- start-up
- shut-down

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:

- Describe how a period of transient operation begins and the ways that it can end
- Set up, simplify and solve the transient CSTR design equations for the quantitative analysis of a given system
- Perform a quantitative analysis of a transient CSTR operation and use the results to describe the system response
- Discuss factors that must be considered when specifying a start-up or shut-down procedure
- Give a few examples of possible ways to start-up or shut-down a CSTR
- Explain why specification of start-up and shut down procedures is an important aspect of the initial design of a reactor system.

Information

Before discussing the particulars of transient analysis, it may be useful to introduce some nomenclature. When one uses the CSTR design equations, one typically knows the inputs to the reactor system: inlet molar flow rates, inlet volumetric flow rate, inlet temperature, inlet pressure, inlet cooling or heating details, etc. The design equations are then solved to find the outlet molar flow rates and the outlet temperature. If the system is operating in a transient mode, then the design equations are solved to find how the values of the outlet molar flow rates and outlet temperature vary with time. The values and/or time variation of the outlet molar flow rates and outlet temperature can be thought of collectively as the

how the system “behaves,” or “performs,” or as the system’s “response.” All the other, known quantities (the inlet flows, inlet temperatures, rate of heat input or removal, etc.) can be collectively thought of as the “operating parameters” for the system. The purpose of a transient analysis of a CSTR system is to determine how the system responds following a change in one or more of its operating parameters. The operating parameters might be changed deliberately, say to shut down the reactor, or changes might be unintended, say due to some upset elsewhere in the facility that affects an operating parameter for the CSTR.

Often we assume that the change in the operating parameter or parameters is made instantaneously. Still, no matter how the change in the operating parameter is made, the transient analysis begins at the instant when the change has just been initiated. In many cases the changes that are made to CSTR processes are step changes in an operating parameter’s value. An inlet reactant concentration is set to a new value or the flow of the heat transfer fluid is adjusted to a new value. There are other kinds of changes that can occur where the operating parameter is made to vary with time in a known manner. One might increase coolant flow linearly over time. For the latter type of change, the transient analysis begins at the instant the forced variation of the operating parameter is initiated.

The preceding discussion may help clarify what a transient analysis is and when it begins, but when does the transient end? Actually, there are three answers to this question. First, the transient analysis will end at the point in time when another change is made to one or more operating parameters. Of course, the system would respond to this new change, and so a new transient analysis would begin as soon as the new change was made. In this regard, the transient analysis of a CSTR is similar to the analysis of a batch reactor where each step in the batch reactor operating protocol is analyzed separately with one step beginning immediately after the other ends. The second way a transient analysis can end is that the system can settle down to a steady state and stop changing with time. Theoretically this takes an infinite period of time, but practically once the system is within a few percent of steady state, the transient can be considered to be complete. Of course a steady state can only be reached if all the operating parameters are constant; a steady state won’t occur, for example, if the coolant flow is being increased linearly over time. The third possibility for the end of the transient period is that it will never end. It is possible for a system to go into periodic oscillations that will never end (unless an operating parameter is changed). This last situation is one that CSTR operators typically try to avoid.

With that as background, we can now consider how to analyze a transient process. At the beginning of an analysis, it’s a good idea to convert all known quantities to a consistent set of units. A mole balance, equation (23.1), is then written for each reactant and product of any reaction occurring in the system, and an energy balance, equation (23.2) is written for the reaction volume. If heat is being added or removed from the reactor via a jacket or coil that contains a heat transfer fluid, it may also be necessary to write an energy balance on that heat transfer fluid. For example, if the heat transfer fluid in the coil or jacket is perfectly mixed, equation (23.3) is the corresponding energy balance for the situation where the heat transfer fluid heat capacity and density are constant. Often there will be quantities appearing in these equations that are zero-valued or negligible for the system under consideration. For example, if the reactor is adiabatic, the heat input term will equal zero or if the only moving shaft or boundary is that of an

agitator, the work term may be negligible. In almost all cases in this course, the reaction volume and the reactor pressure will be constant, so the last two terms on the left side of equation (23.2) will equal zero. These quantities can be eliminated at this point.

$$\frac{V}{\dot{V}}\frac{d\dot{n}_i}{dt}+\frac{\dot{n}_i}{\dot{V}}\frac{dV}{dt}-\frac{\dot{n}_i V}{\dot{V}^2}\frac{d\dot{V}}{dt}=\dot{n}_i^0-\dot{n}_i+V\sum_{\substack{j=\text{ all}\\ \text{reactions}}}\nu_{i,j}r_j \tag{23.1}$$

$$V\left(\sum_{\substack{i=\text{all}\\ \text{species}}}\frac{\dot{n}_i\hat{C}_{p-i}}{\dot{V}}\right)\frac{dT}{dt}-P\frac{dV}{dt}-V\frac{dP}{dt}=\dot{Q}-\dot{W}-\sum_{\substack{i=\text{ all}\\ \text{species}}}\left(\dot{n}_i^0\int_{T^0}^{T}\hat{C}_{p-i}\,dT\right)-V\sum_{\substack{j=\text{all}\\ \text{reaction}}}r_j\Delta H_j\left(T\right) \tag{23.2}$$

$$\frac{dT_e}{dt}=\frac{\dot{m}\tilde{C}_{p,e}\left(T_e^0-T_e\right)-\dot{Q}}{\rho_e V_e\tilde{C}_{p,e}} \tag{23.3}$$

Notice that in the design equations (23.1) through (23.3), there are three more dependent variables, $\dot{n}_i$, T, T_e, V, P and $\dot{V}$, than equations. This may still be true after the zero-valued and negligible terms have been eliminated. If it is, then one must either express the "extra" dependent variables in terms of the other dependent variables (eliminating the derivatives containing the "extra" dependent variables), or add differential equations governing the "extra" dependent variables. The nature of these additional differential equations will depend upon the specific problem being solved.

Once the number of differential equations equals the number of dependent variables, the equations can be solved. Here we will assume that they can be written in the matrix form shown in equation (23.4) where the elements in the vector $\underline{y}$ represent the dependent variables. In these equations, t is the independent variable, and it represents the elapsed time since an operating parameter was changed to start the transient response. As such, the values 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.

$$\frac{d\underline{y}}{dt}=\underline{f}\left(\underline{y},t\right);\quad \underline{y}\left(t=0\right)=\underline{y}^0 \tag{23.4}$$

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 (23.4). No matter what software package you use, when the

equations are written in the form of equation (23.4), 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

As was the case with the batch reactor design equations, the functions, f_i, in the set of design equations are likely to contain constants as well as quantities other than the dependent variables that vary during the transient response. 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 rate expressions in equations (23.1) and (23.2) will likely contain concentrations or partial pressures, and their values will change over time during the transient.

The initial values of the dependent variables must also be provided, and in some situations, this can be confusing. First, remember that the transient analysis begins at the point in time where a change has been made to one or more operating parameters. As a consequence, the only relevant values of the changed operating parameters are the values after the change has been made; the *values of the operating parameters before the change are irrelevant to the transient analysis*. Secondly, it is essential to recognize the difference between an inlet quantity and the initial value of a quantity. In the design equations (23.1) through (23.3) a superscripted zero is used to denote inlet quantities. A close examination of those equations reveals that none of the dependent variables are inlet quantities. The initial values that are needed are the values of the dependent variables at the instant the change in operating parameters occurs. Since the inlet quantities are not dependent variables in the equations, ***the initial** values needed to solve the equations are not the **inlet** values*. For example, consider equation (23.1) for a system with a constant reaction volume and a constant volumetric flow rate. In that case, the dependent variable in the equation is $\dot{n}_i$, the outlet molar flow rate of species i. Therefore, when solving that equation, you must provide the initial value of the *outlet* molar flow rate of species i, not the inlet molar flow rate of species i.

Having determined the initial conditions, the design equations can be integrated to determine the response, that is the values of the outlet molar flow rates and the outlet temperature over time. The transient CSTR design equations can sometimes be “stiff.” This is a mathematical term that won’t be defined or discussed here, but simply noted. If the equations are stiff, one needs to use appropriate numerical methods in order to obtain accurate results. One should consult the manuals for the software being used, an applied mathematician or a good text on numerical methods. The end of the integration will depend upon how the transient ends as discussed earlier. It can go from time zero until the next change is made in an operating parameter. It can go from time zero until one notices that the response has become some sort of sustained oscillation. It can go from time zero until all of the outlet molar flow

rates and the outlet temperature are within a few percent of their steady state values and stabilizing. Of course, in this last case, the steady state values are the ones corresponding to the values of the operating parameters after all changes have been made. In fact, the steady state values can be computed using the methods that were discussed in Unit 22.

Once the design equations have been solved, the results can be used to perform whatever engineering task was assigned. One thing to remember, especially for first time students, is to interpret the physical meaning of the transient response. For example, if one computes that the temperature will rise to 5000 ° in a span of seconds, that might be interpreted to mean that the reactor exploded or otherwise failed.

When a new reactor system is being designed, there are many tasks that need to be performed in addition to sizing the equipment. Two of these are specifying the procedure to be used to start the reactor up and specifying the procedure for the normal (non-emergency) *shut-down* of the reactor. It isn't possible to give one procedure that will work for every CSTR and reaction system. Each system presents its own unique peculiarities and demands. It wouldn't be out of the ordinary, during the design phase for a CSTR system, to perform an analysis of several different start-up and shut-down procedures and then build from those results to eventually reach a final procedure. Additionally, one can often find information on the start-up and shut down of CSTRs being used with similar reactions, and those procedures can be used as an initial point for developing appropriate procedures for the system at hand.

Several factors are important when specifying start-up and shut-down procedures. The first, and most important is safety. It is imperative that the procedure can be performed routinely without endangering plant workers or those living in the surrounding communities. The first safety issue that usually springs to mind is reactor runaway leading to explosion or other catastrophe. If any of the reactions involved in the process are exothermic, this is clearly an issue to be addressed. Additionally, if any of the reagents by themselves are capable of exothermic reaction with air this may necessitate purging the system with an inert gas or solvent prior to start-up. Start-up and shut-down can involve conditions far from those that prevail at steady state, they can involve processing times that are significantly longer than the steady state residence time, and they can involve exposure to additional chemicals (such as air) that are not present at steady state. For these reasons, it is important to have a broad understanding of the chemistry under all these conditions, not just those experienced near steady state. Similarly, in the transient analysis of start-up or shut-down, it is essential that the rate expressions being used are still valid at these conditions far from the steady state conditions.

Of course cost is always a factor. The cost of startup can be minimized by using the fastest start-up procedure possible, within the constraints of safety, regulatory compliance, etc. The faster the reactor comes to steady state, the sooner the process can start making profit. Keeping the start-up process as simple as possible may also help keep costs down since a complex procedure may require more manpower than a simpler process. Simplicity is also beneficial as it makes operator training easier. The efficiency of the start-up or shut-down procedure will also impact its cost. If starting up or shutting down involves a continuous flow of reagents, but doesn't generate a product that can be sold, the cost of the procedure will be higher. Clearly it will waste a significant amount of reagent, but there may also be costs

associated with disposal of the products generated during the procedure, especially if they are not environmentally friendly.

Given those factors and considerations, reactor start-up typically requires doing three things: getting the system temperature from ambient to the steady state operating temperature, getting the process flow rates from zero to their steady state values, and doing these things in a manner that causes the system to arrive at the desired steady state (Unit 24 will show that doing the first two things doesn't guarantee the third will happen). Similarly, shutting down involves stopping the flow and (usually) cooling to ambient temperature. The same considerations are important. There are systems where simply stopping the flow of a reactant into the system will lead to an explosion. Clearly, the shut-down procedures require just as much thought, planning and analysis as the start-up procedures.

Here are a few start-up procedures that one might try, but again, every system has its own peculiarities, and as a design engineer, you should explore multiple potential procedures in order to find the one that is most suitable for the particular system at hand. (It's assumed in the following that the steady state operating conditions are at a temperature greater than ambient.)

- Operate as a batch reactor until conversion nears the desired steady state, then slowly add in the feed and heat transfer.
- Start the feed flow while heating and then adjust heat transfer over time to bring the system to steady state.
- Fill the reactor with a mixture with the desired final steady state composition, then start heating, eventually start flow and adjust heat transfer to bring the system to steady state.
- Heat system to desired operating temperature with one reagent flowing, then gradually add second reagent to the feed while adjusting heat transfer to bring the system to steady state.

These are only a few of many possibilities. Similarly, there are many ways to shut a system down. In some cases it may be possible to simply stop the flow and cool in batch mode, while other systems may require a different procedure.