

A First Course on Kinetics and Reaction Engineering

Unit 22. Analysis of Steady State CSTRs

Overview

Reaction engineering involves constructing an accurate mathematical model of a real world reactor and then using that model to perform an engineering task or analysis. Unit 22 examines setting up and solving models for steady-state CSTRs. CSTRs are often designed to operate at steady state, producing a time-invariant flow of product at constant temperature and composition. A systematic procedure for the analysis of CSTR is suggested, with the caveat that deviations from this procedure may sometimes be required, depending upon the particular system being modeled.

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:

- Recognize problems wherein the reactor can be modeled as a CSTR
- Formulate the CSTR design equations needed to model or design a specific CSTR
- Solve the steady state CSTR design equations and use the results to perform requested reaction engineering or design tasks

Information

It can be helpful when setting up a steady-state CSTR model to make a sketch or schematic diagram of the system such as that given in Figure 22.1. Every reaction taking place within the reactor should be identified, numbered, and then written down along with its rate expression as shown in Figure 22.1, directly above the cartoon of the reactor. (No rate expression is given in Figure 22.1; when solving a problem, the rate expression would appear at the end of the information at the top of the figure.) If any shorthand is going to be used, it should be introduced at this point. That is, if the reactions involve complicated chemical formulae, one might prefer to use A, B, etc. in place of the chemical formulae. If this is done, it is a good idea to create a key that relates the shorthand to the actual chemical formulae. The schematic drawing should indicate the inlet stream (or streams), and for each such stream it should list the volumetric flow rate, temperature, pressure, and molar flow rate of each species in that stream. In this course, quantities with a dot above them represent flow rates, and here a superscripted zero after the variable denotes an inlet stream quantity. It is assumed that there is a single feed stream and a single effluent stream. The schematic should similarly indicate the outlet stream with the same information. Finally, the schematic should indicate the dimensions and properties of the reactor including the fluid volume and parameters associated with heat transfer. An alternative to listing all the heat transfer variables would be simply to list the rate of heat flow to the system, \dot{Q} , if that is all that is needed to perform the assigned task or analysis. If there is any significant shaft work associated with the reactor,

this should be indicated in the schematic, too. As the schematic diagram is generated, any quantities that are known can be converted to a consistent set of units and recorded directly on the schematic next to the variable used to represent that quantity. When the value of a quantity is unknown, only the variable is entered on the schematic.

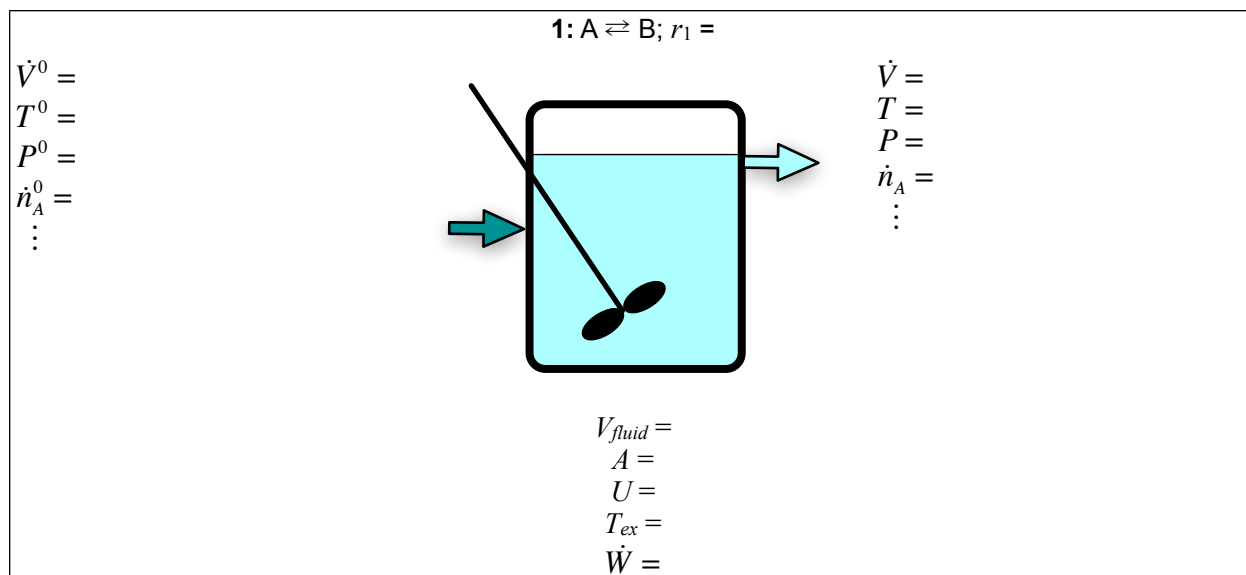


Figure 22.1. A schematic diagram that can be useful when setting up a model for a steady-state CSTR.

The next thing that needs to be done is to gather and tabulate physico-chemical data that may be needed in the model. This includes heat capacities (either for each species or sometimes for the fluid phase as a whole), standard enthalpies and free energies of reaction, densities, etc. Once these data have been accumulated, a thermodynamic equilibrium analysis should be performed to ascertain whether the reaction(s) is(are) reversible or irreversible. The rate expression for each reversible reaction should be checked to ensure that it properly predicts the net rate to equal zero whenever the environmental variables correspond to their equilibrium values. If the rate expressions do not properly go to zero at equilibrium, they can be forced to do so as discussed in Unit 5. Alternatively, one can perform kinetics experiments to find a rate expression that does properly predict a net rate of zero at thermodynamic equilibrium.

In creating the schematic, every chemical species present in the system should have been identified and its flow rate listed for each inlet and outlet stream. At this point, a steady-state CSTR mole balance should be written for each reactant and product of any reaction taking place in the system. A mole balance can also be written for inert species, if desired. Recall from Unit 17 that the steady-state mole balance design equation for a CSTR takes the form of equation (22.1). In addition to the mole balances for each of the reactants and products, a steady-state energy balance design equation should also be written, as given in equation (22.2), which also was derived in unit 17 where it was assumed that the fluid is ideal solution. As was the case with batch reactors, the summation of sensible heats for the

individual species (first term on the right side of equation (22.2) may be replaced with an expression for the reacting fluid as a whole, if appropriate - see below).

$$0 = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all \\ \text{reactions}}} \nu_{i,j} r_j \quad (22.1)$$

$$0 = \sum_{\substack{i=all \\ \text{species}}} \left(\dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} dT \right) + V \sum_{\substack{j=all \\ \text{reactions}}} r_j \Delta H_j(T) - \dot{Q} + \dot{W} \quad (22.2)$$

At this point, any quantities appearing in the design equations that are known to be negligible or equal to zero should be eliminated. For example, if the reactor is being operated adiabatically, then \dot{Q} will equal zero. Similarly, if the only shaft or moving boundary is the shaft of the agitator, the rate of doing work, \dot{W} , can be set to zero. (Under unusual circumstances, such as a highly viscous fluid, this term might not equal zero, but normally the work associated with the agitator is negligible in comparison to other energy terms in a CSTR). If the reactor is not adiabatic, an expression relating \dot{Q} to the heat transfer coefficient, heat transfer area and heat transfer fluid temperature(s) can be substituted into the energy balance design equation. Perry's Chemical Engineering Handbook [1] is a good starting place for finding appropriate heat transfer correlations. If the heat capacity and heat of reaction data being used take the form of equations (e. g. the Shomate equations), these can also be substituted into the energy balance design equations at this time.

It may also be possible or necessary to write an energy balance on the heat transfer fluid. The only situations to be considered here are the same as those used with a batch reactor: a heat transfer fluid that only undergoes a phase change and a perfectly mixed heat transfer fluid that only gains/loses sensible heat. The energy balances for these situations are the same as they were for a batch reactor (see Unit 19). This unit only considers steady state CSTR, so the term for the accumulation of sensible heat in the energy balance on the perfectly mixed heat transfer fluid will equal zero, leading to equation (22.3). The corresponding expression for the heat flow, for either case, is given by equation (22.4).

$$0 = \dot{m} \tilde{C}_{p,e} (T_e^0 - T_e) - \dot{Q} \quad (22.3)$$

$$\dot{Q} = UA(T_e - T) \quad (22.4)$$

It also will be necessary to relate the composition variables that appear in the rate expression(s) to the species molar flow rates that appear in the design equations. Specifically, if partial pressures appear in the rate expressions, equation (22.5) can be used to relate the partial pressures to the molar flow rates, providing that the fluid behaves as an ideal gas. Similarly, if concentrations appear in the rate expressions, equation (22.6) can first be used to relate the concentrations to the molar flow rates. If the fluid phase is a liquid, it can often be assumed to be of constant density in which case equation (22.7) can

be used, and if the fluid phase is an ideal gas, equation (22.8) can be used. Additionally, in a CSTR, the pressure drop through the reactor is usually negligible so that one can set P^0 equal to P .

$$P_i = \frac{\dot{n}_i}{\sum_{k = \text{all species}} \dot{n}_k} P \quad (22.5)$$

$$C_i = \frac{\dot{n}_i}{\dot{V}} \quad (22.6)$$

$$\dot{V} = \dot{V}^0 \quad (\text{constant density liquid}) \quad (22.7)$$

$$\dot{V} = \frac{RT \left(\sum_{k = \text{all species}} \dot{n}_k \right)}{P} \quad (\text{ideal gas}) \quad (22.8)$$

Upon noting that the composition variables in the rate expressions can be related to the outlet molar flow rates, there generally will be a total of N design equations where N is equal to the number of mole balances plus one. In order to solve this set of non-linear algebraic equations, there needs to be exactly N unknown quantities appearing in the equations. If the equations are found to contain more than N unknown quantities, then the system specification should be examined for any additional information that was not entered into the schematic diagram. One common situation that might arise is that the conversion of a particular species or a selectivity might have been specified. Specifications like these can be interpreted to mean that one outlet molar flow rate is not an unknown. In the case of a specified conversion, the outlet molar flow rate of the species is known in terms of its inlet molar flow rate, equation (22.9). Similarly in the case of a selectivity for one species relative to another, the outlet molar flow rate of that species is known in terms of the other, equation (22.10).

$$\dot{n}_i = \dot{n}_i^0 (1 - f_i) \quad (22.9)$$

$$\dot{n}_i = S_{ij} \dot{n}_j \quad (22.10)$$

It is possible, even after all the additional system specifications have been added as equations, that there will still be one more unknown than the total number of equations. This will happen if every one of the reactor system specifications is given as an intensive variable. As was noted in the case of the batch reactor, this means that none of the specifications is sufficient to fix the size of the system being analyzed. If this is the case, then it is permissible to assume a basis for the analysis. To do so, one simply chooses a value for any one extensive variable such as the reaction volume, the inlet molar flow rate of any one species, the inlet volumetric flow rate, etc. All extensive results obtained from the subsequent engineering analysis will only apply for the particular basis chosen, but all intensive results will apply to a system of any size.

The steady-state CSTR model is properly formulated when the number of non-differential design equations is just equal to the number of unknown quantities appearing in those equations, as indicated in

equation (22.11), where z_1 through z_n represent the unknown quantities. Once the model is properly formulated, it can be solved and used to perform whatever engineering task or analysis was originally requested. While some simple models can be solved analytically, it will usually be necessary to use a numerical solution method.

$$\begin{aligned} 0 &= f_1(z_1, z_2, \dots, z_n) \\ 0 &= f_2(z_1, z_2, \dots, z_n) \\ &\vdots \\ 0 &= f_n(z_1, z_2, \dots, z_n) \end{aligned} \tag{22.11}$$

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 S2 presents a brief introduction to the numerical solution of non-differential equations; if you aren't familiar with numerical solution of such equations, you should read Supplemental Unit S2. If you plan to use MATLAB to solve the design equations, Supplemental Unit S2 also presents template files that can be used to solve sets of non-differential equations of the form given in equation (22.11). No matter what software package you use, when the equations are written in the form of equation (22.11), you typically will need to provide two things as input to the software:

- Code that evaluates the functions, f_1 through f_n , given values of the unknown variables, z_1 through z_n
- A guess for the solution, that is, for the values of z_1 through z_n that cause all of the functions, f_1 through f_n , to equal zero.

As noted at the start of this unit, the procedure given here is general and may sometimes need to be adapted for a particular system analysis. One such case is that of an isothermal reactor; when a CSTR operates isothermally, the mole balance design equations can often be solved independently without ever writing an energy balance equation. This is more of a textbook or classroom situation than a real-world situation. In the real world, one would need to know the rate of heat addition or removal that is necessary to operate isothermally, and consequently one would need the energy balance. It is very common, however, to find textbook problems for isothermal reactors that can be solved without using an energy balance. Indeed, sometimes the problem statement does not provide sufficient information to solve the combined mole and energy balances, but it does provide enough data to solve the mole balances independently.

The other common modification to the general process given here was alluded to previously. Specifically, equation (22.2) above writes the sensible heat in terms of the molar heat capacities of the individual species. Sometimes, especially when a solvent is used, the heat capacity of the solution is nearly, independent of the composition, though it still may depend upon temperature. This can happen because the heat capacity of the solvent predominates relative to the heat capacities of the solutes. In cases like this, the sensible heat term in equation (22.2) might need to be replaced with a term

expressing the sensible heat in terms of the heat capacity of the fluid as a whole. Often this will be a mass heat capacity, but a volume heat capacity might be encountered, too. Table 22.1 gives three different ways the sensible heat might be included in the energy balance equation (22.2).

Table 22.1 Sensible heat terms that might appear in the energy balance equation.

Situation	Sensible Heat Term
Molar specific heat capacities of the species, \hat{C}_{pi}	$\sum_{\substack{i=all \\ species}} \left(\dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} dT \right)$
Mass specific heat capacity of the solution, $\tilde{C}_{p,soln}$	$\dot{V}^0 \int_{T^0}^T \rho_{soln} \tilde{C}_{p,soln} dT$
Volume specific heat capacity of the solution, $\hat{C}_{p,soln}$	$\dot{V}^0 \int_{T^0}^T \hat{C}_{p,soln} dT$

One final situation that would require a modification to the general approach presented in this unit is a system where the full spectrum of products is not known or is not measurable. An example of a system like this is a polymerization reaction where literally hundreds of thousands of slightly different products are formed. There are a variety of approaches that can be used with this type of system. One approach that sometimes can be used is to simply use a balance on the reactant and see whether the resulting design equation can be solved, perhaps in combination with a simplified energy balance. There are a number of more advanced ways to model such reactions, but they will not be considered in this course.

References Cited

1. Perry, R.H. and C.H. Chilton, eds., *Chemical Engineer's Handbook*. 5th ed. McGraw-Hill Chemical Engineering Series. 1973, McGraw-Hill: New York.