PART
2

Control of Individual Units

CHAPTER 4

Reactors

4.1 Introduction

In Chap. 2 we illustrated the issues of plantwide control by using very simple unit operations. In each example, the reactor was a well-mixed, liquid-filled tank where we carried out isothermal, elementary reaction steps. A level control loop was sufficient to make the reactor fully functional. The point we tried to convey is that no matter how simple the individual unit operations (and their controls) may be, new control issues arise when the units become part of an integrated plant. Certainly these issues are still present when we introduce more complexity into the individual processing steps. In this chapter we study some industrially relevant reactor systems.

There is a vast literature on chemical kinetics and reactor engineering, but relatively little has been written on the practical aspects of industrial reactor control. Given the importance of reactors in chemical processing plants, this situation is surprising. One explanation might be that reactors are highly nonlinear so the bulk of control theory (which is for linear systems) does not readily apply. Another reason could be that many reactors are modeled as distributed systems (e.g., plug-flow reactors) and the models don't lend themselves to compact transform analysis. One can also argue that reactor control invariably involves plantwide process control, thereby significantly extending the scope of any study. Finally, many industrially important reactor systems have not been published in the open literature because they have proprietary designs and control systems.

Whatever the reasons may be for the lack of references on reactor control, we found ourselves in a difficult position in writing this chapter. The initial intent was to give a brief overview of the subject and show some typical unit operation control strategies to be used in Step 8 of our plantwide control design procedure. We would have liked to refer elsewhere regarding the details of the various control schemes. Having to abandon this approach, we concluded that a methodology toward reactor control would be a desirable substitute. A methodology has the advantage of being independent of the particular kinetic system and reactor type under consideration.

The methodology we adopt is the one developed by Reuel Shinnar and his coinvestigators. It has been described in a series of papers by Arbel et al. (1995a, 1995b, 1996, 1997). The approach revolves around four areas of activity: reactor modeling, study of open-loop reactor behavior, control structure selection, and use of process design to affect controllability. In their papers, Arbel et al. have illustrated their approach on a complex unit, a fluidized catalytic cracker. We have avoided merely reporting their results and instead tried to be additive by providing examples around much simpler systems such as CSTRs and plug-flow reactors.

The methodology on reactor control assumes some familiarity with reactor engineering. Process engineers and reactor design specialists already have mastered the fundamentals of reaction thermodynamics and kinetics but we were not sure that all control engineers felt equally comfortable with these topics. We have therefore taken the liberty of including a section on fundamentals that covers the elements of reactor engineering. The material for this section has been borrowed from the many excellent textbooks on the subject. We have found the short text by Denbigh and Turner (1971) and the more extensive work by Froment and Bischoff (1979) particularly useful. However, if this feels like old hat to you, please skip directly to the sections on models and open-loop behavior of reactors where we start the design methodology.

4.2 Thermodynamics and Kinetics Fundamentals

4.2.1 Thermodynamic constraints

Chemical reactions can occur provided the reaction products have a lower energy content than the reactants. This is analogous to a ball rolling down an incline. The ball can keep rolling as long its potential energy is lowered from the motion. The "potential" energy for a chemically reacting system, held at a constant temperature, is the Gibbs free energy G, which equals the total energy of the system minus the portion unavailable for mechanical work (see App. A for more details).

$$G = U + PV - TS = H - TS \tag{4.1}$$

where U = internal energy
P = pressure
V = system volume
T = absolute temperature
S = entropy
H = enthalpy

A reaction's ability to proceed at a constant temperature T hinges on a negative change in the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \tag{4.2}$$

where ΔG = Gibbs free energy change due to reaction
ΔH = enthalpy change due to reaction
ΔS = entropy change due to reaction

A system may continue to react as long as the Gibbs free energy keeps decreasing ($\Delta G < 0$). This might occur, for example, when the chemical bonds in the products are stronger than those in the reactants. Such reactions are exothermic and proceed with a heat release. An example is the formation of benzene and methane from toluene and hydrogen mentioned in Chap. 1 for the HDA process:

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \tag{4.3}$$

$$\Delta H^0 = -42.2 \text{ kJ/mol}$$

where ΔH^0 is the heat of reaction at standard conditions (e.g., pure gaseous components at $T = 298$ K and $P = 1$ atm)

Another example discussed in more detail in this book (Chap. 11) is the formation of vinyl acetate from ethylene, acetic acid, and oxygen. This reaction is highly exothermic due to the strong and stable bonds in the water molecules.

$$C_2H_4 + CH_3COOH + {}^1\!/_2O_2 \rightarrow CH_2 = CHOCOCH_3 + H_2O \tag{4.4}$$

$$\Delta H^0 = -176.4 \text{ kJ/mol}$$

While exothermic reactions are often thermodynamically favored, a negative enthalpy of reaction is not necessary. A reaction can also occur when $\Delta H > 0$ (endothermic reaction), provided that there is a large enough increase in the entropy of reaction ($\Delta S > 0$) at constant temperature. An example is the catalytic cracking of heavy petroleum fractions into gasoline, middle distillates, and light olefins. Here it takes a considerable amount of energy to break the carbon-to-carbon bonds in the heavy oil components but the energy gets distributed over a large number of small molecules, thus decreasing "order" and increasing entropy.

Since the entropy increases in most cracking operations, we might expect that it decreases for synthesis reactions. Indeed, this is often the case. A typical example is a polymerization reaction where a large number of monomer units organize in chains, thus reducing the entropy at constant temperature. Whenever a reaction is accompanied by a reduction in entropy, it must be exothermic. This follows from Eq. (4.2), since the Gibbs free energy can be negative for a decrease in entropy ($-T\Delta S > 0$) only when the enthalpy change is negative. Since synthesis reactions are far more common than cracking operations in the chemical industry, we can understand why exothermic reactions dominate in this area.

Exothermic reactions with a decrease in entropy reach equilibrium ($\Delta G = 0$) at some temperature and reverse beyond this point. This is evident from Eq. (4.2) where the negative term ΔH will cancel with the positive term $-T\Delta S$ when T gets sufficiently large. Since we already noted that such reactions are common in the chemical industry, should we expect most reactions to be reversible? In principle, yes, but in practice we operate many reactors at a temperature far below the equilibrium point and therefore never notice any influence of the reverse reaction. There are, however, industrially important exceptions to this rule. The manufacture of ammonia from nitrogen and hydrogen and the formation of sulfur trioxide from sulfur dioxide and oxygen are two prominent cases.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\Delta H^0 = -91.8 \text{ kJ/mol}$$

$$\Delta S^0 = -0.198 \text{ kJ/mol} \cdot \text{K}$$

$$T_e = 91.8/0.198 = 464 \text{ K}$$

$$SO_2 + {}^1\!/_2O_2 \rightleftharpoons SO_3$$

$$\Delta H^0 = -98.9 \text{ kJ/mol}$$

$$\Delta S^0 = -0.094 \text{ kJ/mol} \cdot \text{K}$$

$$T_e = 98.9/0.094 = 1052 \text{ K}$$

where ΔS^0 = entropy change due to reaction at standard conditions (e.g., gases at 298 K, 1 atm)
T_e = equilibrium temperature based on standard state properties

Ammonia and sulfur trioxide reactors must be designed and operated such that the heat of reaction does not raise the reactor temperature enough to cause the reaction to reach equilibrium and therefore stop. The same applies to the reversible isomerization reaction studied in Chap. 9.

We conclude that most reaction systems in the chemical industries are exothermic. This has some immediate consequences in terms of unit operation control. For instance, the control system must ensure that the reaction heat is removed from the reactor to maintain a steady state. Failure to remove the heat of reaction would lead to an accumulation of heat within the system and raise the temperature. For reversible reactions this would cause a lack of conversion of the reactants into products and would be uneconomical. For irreversible reactions the consequences are more drastic. Due to the rapid escalation in reaction rate with temperature we will have reaction runaway leading to excessive by-product formation, catalyst deactivation, or in the worst case a complete failure of the reactor possibly leading to an environmental release, fire, or explosion.

4.2.2 Reaction rate

Thermodynamics tells us whether a chemical reaction is possible but it does not say how fast the reaction goes. For example, the Gibbs free energy favors the formation of water from hydrogen and oxygen at room temperature and atmospheric pressure ($\Delta G^0 = -228.6$ kJ/mol). However, a mixture of these gases can remain in a flask for a long time at room temperature without any noticeable water formation. The problem is that the molecules don't have enough velocity at room temperature to overcome the reaction's activation energy. It takes a spark or a catalyst to make the reaction go at any appreciable speed. When initiated with a spark the exothermic reaction generates enough heat to elevate the temperature of the entire mixture such that the reaction proceeds with explosive speed.

In general, the rate of a reaction depends upon the activation energy and temperature in an exponential fashion:

$$r = k \cdot f(C_i) \tag{4.5}$$

$$k = A_f e^{-E_a/RT} \tag{4.6}$$

where r = specific rate of reaction (mol/L · s)
k = overall rate constant
$f(C_i)$ = function of concentration C_i for reacting species
A_f = pre-exponential factor
E_a = activation energy (kJ/mol)
R = universal gas constant (8.31 J/mol · K)

The significance of the activation energy from a control standpoint is that it dictates to what extent temperature plays a dominant role on the reaction system. To explore this relation we can evaluate the temperature derivative of Eq. (4.5):

$$\frac{dr}{dT} = f(C_i)\frac{dk}{dT} = r\frac{E_a}{RT^2}$$

$$\frac{dr/r}{dT} = \frac{E_a}{RT^2} \tag{4.7}$$

We see that the relative increase in rate per degree change in temperature is proportional to the activation energy. This means that reactions with large activation energies increase their rates more rapidly with temperature than reactions with low activation energies. For example, the activation energy for the vinyl acetate reaction [Eq. (4.4)] is 30.5 kJ/mol. Parallel to the main reaction is also a side combustion reaction consuming some of the ethylene reactant to produce carbon dioxide:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{4.8}$$

The activation energy for the side reaction is 84.1 kJ/mol, making it nearly 3 times more responsive to temperature than the main reaction. At 453 K, where the side reaction starts playing an important role, this translates to a 5 percent increase in the side reaction per kelvin compared to less than 2 percent for the main reaction. At very high temperatures the side reaction completely dominates the picture. Control and optimization of reactor temperature is essential for economic operation.

While reactor temperature often plays a dominant role on reaction rate, it is not the only contribution to the rate expression. We also have the influence of the concentrations of the reacting species as symbolized by $f(C_i)$ in Eq. (4.5). This expression can range from simple to very complex. In the simplest form the rate of reaction is proportional to the reactant concentrations raised to their stoichiometric coefficients. This is true for an elementary step where it is assumed that the molecules have to collide to react and the frequency of collisions depends upon the number of molecules in a unit volume. In reality, matters are far more complicated. Several elementary steps with unstable intermediates are usually involved, even for the simplest overall reactions. When the intermediates are free radicals, there can be a hundred or more elementary steps. From an engineering viewpoint it is impractical to deal with scores of elementary steps and intermediates and we usually seek an overall rate expression in terms of the stable, measurable (in principle) components in the reactor. In theory we can derive such an expression from a known set of elementary steps but in practice we are well-advised to use experimental data to develop reliable rate expressions.

As an example of the often unintuitive nature of many rate expressions, we examine the vinyl acetate reaction. If this reaction took place as a series of simple elementary steps resulting from gas phase collisions of the reactants, the rate expression would be proportional to the reactant concentrations raised to their stoichiometric coefficients.

$$r_{\mathrm{el}} = kC_{\mathrm{E}}C_{\mathrm{A}}C_{\mathrm{O}}^{0.5} \tag{4.9}$$

$$= k(RT)^{-2.5}p_{\mathrm{E}}p_{\mathrm{A}}p_{\mathrm{O}}^{0.5}$$

where r_{el} = rate based on "elementary" kinetics
p_i = partial pressure of component i
E = ethylene
A = acetic acid
O = oxygen

In reality the reaction is carried out over a solid catalyst and probably involves numerous elementary steps and intermediates. As a result the actual rate expression found by fitting experimental data looks quite a bit different than Eq. (4.9):

$$r_{ex} = k\,\frac{p_{\mathrm{E}}p_{\mathrm{A}}p_{\mathrm{O}}(1 + 1.7p_{\mathrm{W}})}{[1 + 0.583p_{\mathrm{O}}(1 + 1.7p_{\mathrm{W}})](1 + 6.8p_{\mathrm{A}})} \tag{4.10}$$

where r_{ex} = rate based on empirical expression fitted to experimental data and p_{W} = partial pressure of water. Notice that the partial pressure of water enters the empirical rate expression. Water is a product and does not participate as a reactant in the chemistry. We would never expect it to enter an elementary expression such as Eq. (4.9). The fact that it enters into the empirical expression must be viewed in light of the reaction occurring over a catalyst. It is conceivable that water somehow promotes the catalyst activity.

From a control standpoint it is important to know the actual form of the kinetic rate expression. The reason is that it dictates which reactant and product components play a dominant role on the behavior of the reactor. For example, components with a nonzero exponent play a direct and predictable role especially at low concentrations. But even components that don't enter the rate expression (e.g., inerts) play an indirect role by their influence on the concentrations of the reactants. This secondary effect is much less predictable for a multicomponent system. In general, it is seldom easy to determine the composition effects of a single component from a superficial look at the reaction and its stoichiometry. Instead, the best available kinetic rate equation should be incorporated into a reactor model (steady-state or dynamic). With this model we then can evaluate the integrated effects of temperature and species compositions. For example, from the overall stoichiometry of the vinyl acetate reaction we would expect that an increase in the partial pressure of acetic acid should increase the total production rate. This turns out to be incorrect because the rate is close to zero order in acetic acid partial pressure due to cancellation effects with the denominator in Eq. (4.10). Acetic acid can therefore not be counted as a dominant variable for the control of a vinyl acetate reactor with the kinetic expression derived from the given experimental data.

In most rate expressions the dominant components are reactants. Occasionally we encounter reactions that are dominated by a product. Such reactions are said to be *autocatalytic*. A simple example of an autocatalytic scheme is

$$A + 2B \rightarrow 3B + C$$

with a rate expression

$$r = kC_B^2 C_A \tag{4.11}$$

Since we make one extra mole of component B for every two moles of B consumed, and the rate is highly dependent on the concentration of B, the product dominates the reactor behavior especially at low concentrations.

4.2.3 Multiple reactions

In most industrially relevant reacting systems, one main reaction typically makes the desired products and several side reactions make by-products. The specific rate of production or consumption of a particular component in such a reaction set depends upon the stoichiometry and the rates. For example, assume that the main reaction for making vinyl acetate, Eq. (4.4), proceeds with a rate r_1 (mol/L · s) and that the side reaction, Eq. (4.8), proceeds with rate r_2 (mol/L · s). Then the net consumption of ethylene is $(-1)r_1 + (-1)r_2$ (mol/L · s). Similarly, the net consumption of oxygen is $(-0.5)r_1 + (-3)r_2$, and the net production of water is $(1)r_1 + (2)r_2$. For a given chemistry (stoichiometry), our ability to control the production or consumption of any one component in the reactor is thus limited to how well we can influence the various rates. This boils down to manipulating the reactor temperature and/or the concentrations of the dominant components. Occasionally, the reaction volume for liquid-phase reactions or the pressure for gas-phase reactions can also be manipulated for overall production control. These are the fundamentals of reactor control.

4.2.4 Conversion, yield, and selectivity

While the individual reaction rates are the variables that can be affected in a reacting system, we often express the performance of the reactor in terms of measures derived from the rates. Conversion and yield are such quantities. Conversion refers to the fractional consumption of a reactant in the reactor feed, whereas yield refers to the amount of product made relative to the amount of a key reactant fed to the reactor. In recycle systems the per-pass conversion of the various reactants is a relevant measure. It depends upon the rate of reaction for the specific component but also on the reactor feed. The per-pass conversion of an excess reactant is less than that of a limiting reactant. For example, the per-pass conversion of ethylene in a typical vinyl acetate reactor is only 7 percent whereas the per-pass conversion of oxygen is 36 percent. In Chap. 2 we discussed the plantwide control implications of incomplete conversion.

Selectivity is a measure similar to yield in that it tells how much desirable product is made from a reactant. Selectivity is particularly informative for parallel reactions involving the same key reactant. Here it measures what proportion of the converted reactant goes to useful products. In the production of vinyl acetate, for example, ethylene reacts in the main reaction as well as in the side reaction. The selectivity of ethylene to vinyl acetate is

$$\text{SEL} = 100\,\frac{\text{mol/s vinyl acetate produced}}{\text{mol/s vinyl acetate produced} + 0.5\ \text{mol/s}\ \text{CO}_2\ \text{produced}}$$

4.3 Fundamentals of Reactors

4.3.1 Types

The simplest type of reactor we can imagine is an adiabatic batch reactor. In such a system we charge the reactants, close the vessel, and let the mixture react for a certain amount of time. The progress of such a reaction depends upon the initial conditions of the batch and the kinetic rate expressions. For a sufficiently long batch time relative to the reaction rates, the system ends up at a unique steady state. This steady state is a thermodynamic equilibrium state due to the Gibbs free energy reaching a minimum (isothermal reactor) or the entropy reaching a maximum (adiabatic operation).

While the adiabatic batch reactor is important and presents many control issues in its own right, we are concerned here primarily with continuous systems. We consider in detail two distinct reactor types: the continuous stirred tank reactor (CSTR) and the plug-flow reactor. They differ fundamentally in the way the reactants and the products

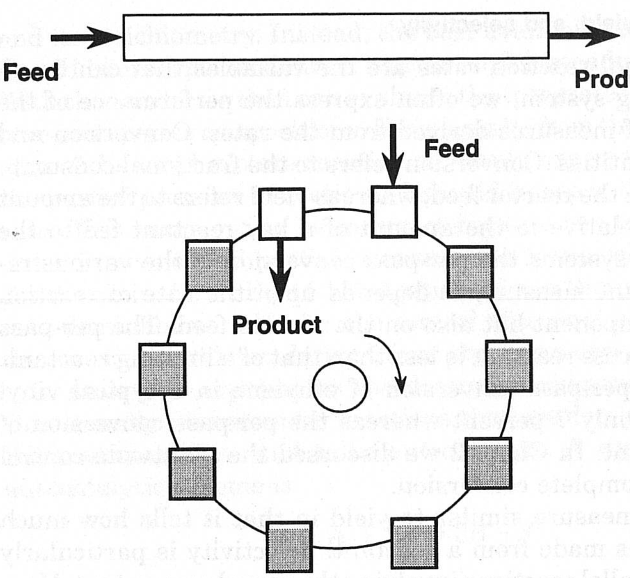

Figure 4.1 Plug-flow reactor represented as sequence of small batch reactors.

are backmixed within the reactor. The plug-flow reactor shown schematically in Fig. 4.1 has no backmixing between compartments of the reactor. An ideal plug-flow reactor can be visualized as a "conveyor system" of small adiabatic batch reactors that are charged with fresh feed, allowed to react in isolation, and then discharged at the end of the cycle (Fig. 4.1). Each little reactor in the system will have its own composition and temperature depending only upon the initial conditions (the fresh feeds), the batch time, the thermodynamics, and the kinetics of the system.

Instead of discharging all the material from each little batch reactor in Fig. 4.1, imagine now that we leave some material in the reactor to be mixed with the fresh feed (Fig. 4.2). Diluting the fresh feeds will alter the reaction rate. In addition, we must run the conveyor system faster to make up for the reduced space in the reactors. These two factors change the reactor output such that it is no longer simply determined by the fresh feed conditions and the batch time but depends upon the recycle ratio as well. We can, however, eliminate the explicit mention of the recycle ratio from the system description by recycling everything (complete backmixing) and running the conveyor system infinitely fast. All the small batch reactors now have the same composition and temperature. This is a simple analog of a CSTR where the backmixing is typically done by agitation, sparging, or fluidization as in Fig. 4.3.

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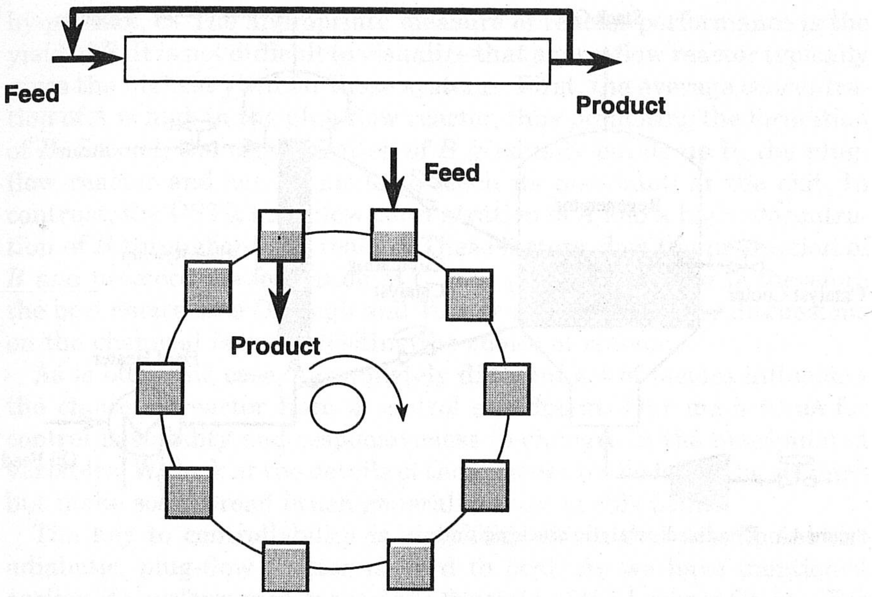


Figure 4.2 Plug-flow reactor with recycle.

The CSTR and the tubular reactor are idealized extremes on the mixing spectrum. Industrial reactors usually fall somewhere in between. For example, diffusion, conduction, convection, and flow channeling can make a plug-flow reactor have less than ideal composition and temperature profiles. Similarly, insufficient agitation in a CSTR can create channeling that alters its homogeneous composition and temperature assumption. Some industrial reactors can be viewed as hybrids between a CSTR and a plug-flow reactor. For example, a fluidized bed can be considered backmixed in the solid phase whereas the plug-flow assumption is frequently valid for the gas phase. The same

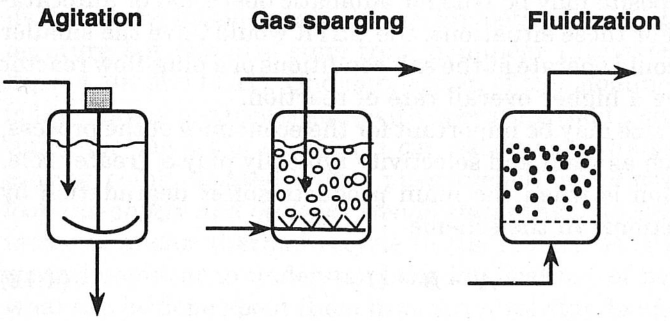


Figure 4.3 Continuous stirred tank reactors.

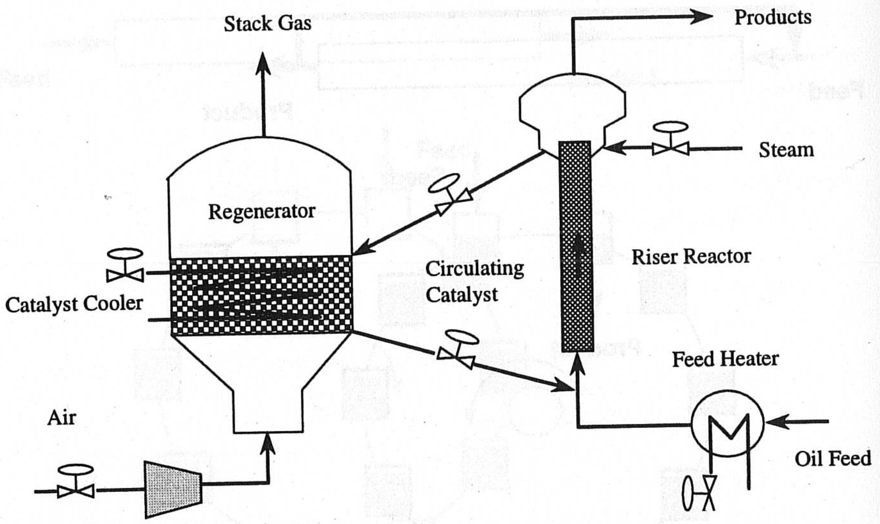


Figure 4.4 Fluidized catalytic cracking unit.

can be said about sparged gas-liquid reactors. More complex reactor systems can be constructed by combining plug-flow and backmixed units. For example, in Fig. 4.4 we show a schematic of a fluidized catalytic cracker that can be viewed as a plug-flow reactor (the riser reactor) coupled to a CSTR (the regenerator).

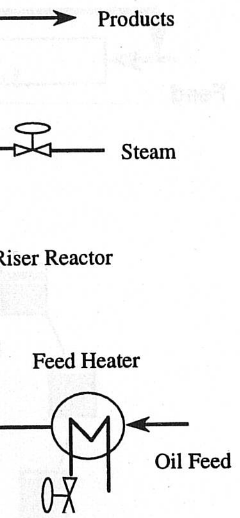
4.3.2 Reactor selection

The primary reason for choosing a particular reactor type is the influence of mixing on the reaction rates. Since the rates affect conversion, yield, and selectivity we can select a reactor that optimizes the steady-state economics of the process. For example, the plug-flow reactor has a smaller volume than the CSTR for the same production rate under isothermal conditions and kinetics dominated by the reactant concentrations. The opposite may be true for adiabatic operation or autocatalytic reactions. For those situations, the CSTR would have the smaller volume since it could operate at the exit conditions of a plug-flow reactor and thus achieve a higher overall rate of reaction.

While reactor size may be important for the economics of the process, other factors such as yield and selectivity typically play a greater role. A classic situation is when the main products suffer degradation by consecutive reactions. In the scheme

$$A \rightarrow B \rightarrow C \qquad (4.12)$$

we are interested in the product, B, and would like to minimize the



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by-product, C. The appropriate measure of reactor performance is the yield of B. It is not difficult to visualize that a plug-flow reactor typically gives the highest yield for these systems. First, the average concentration of A is high in the plug-flow reactor, thus promoting the formation of B. Second, the concentration of B gradually builds up in the plug-flow reactor and can be made to reach its maximum at the exit. In contrast, the CSTR has a low concentration of A and a high concentration of B throughout the reactor. These factors slow the production of B and promote the formation of C. The plug-flow reactor is therefore the best choice. See Denbigh and Turner (1971) for further discussions on the chemical factors affecting the choice of reactor.

As is often the case, a completely different set of factors influences the choice of reactor from a control standpoint. Our main focus for control is stability and responsiveness to changes in the manipulated variables. We look at the details of these issues in the following sections but make some broad brush generalizations at this point.

The key to controllability is simplicity. From that standpoint the adiabatic, plug-flow reactor is hard to beat. As we have mentioned earlier, its performance is a unique function of the feed conditions. For isothermal operation of exothermic reactions, the CSTR is first in line. The reason is that there is only one temperature and one set of compositions to control as opposed to the profiles that govern tubular reactors. In addition, the cooled plug-flow reactor can be very sensitive to operating parameters. Beyond this it is hard to generalize. This is why we feel that a methodology toward reactor control is the best approach, as we described in the introduction to this chapter. This methodology begins by characterizing the open-loop behavior of reactors.

4.4 Models

4.4.1 Introduction

Chemical reactors are inherently nonlinear in character. This is primarily due to the exponential relationship between reaction rate and temperature but can also stem from nonlinear rate expressions such as Eqs. (4.10) and (4.11). One implication of this nonlinearity for control is the change in process gain with operating conditions. A control loop tuned for one set of conditions can easily go unstable at another operating point. Related to this phenomenon is the possibility of *open-loop instability* and *multiple steady states* that can exist when there is material and/or thermal recycle in the reactor. It is essential for the control engineer to understand the implications of nonlinearities and what can be done about them from a control standpoint as well as from a process design standpoint.

To study issues related to nonlinearities we need nonlinear models. In principle there is no difficulty in finding all the equations that can go into a model for an arbitrary reactor. Textbooks on reaction engineering do a great job in covering the basics as well as the details. The trick is to produce a practical model in the sense that it is computationally efficient and yet provides the required insights about the system. This is unfortunately still an art. In this respect we refer to two excellent papers by Shinnar (1978, 1981). Other useful references to dynamic modeling are Luyben (1990) and Arbel et al. (1995a).

We will take a closer look at one of the simplest systems conceivable, a constant-volume and -density, cooled CSTR with a first-order, irreversible reaction $A \rightarrow B$. While this model is quite simple it still contains most of the relevant issues surrounding an open-loop, nonlinear reactor. Referring to Fig. 4.5, this system can be described by one component balance and one energy balance:

$$V\frac{dC_A}{dt} = F(C_{A0} - C_A) - rV \tag{4.13}$$

$$\begin{aligned}(V\rho C_P + M_w C_w)\frac{dT}{dt}\\ = F\rho\,(C_{P0}T_0 - C_P T) - UA(T - T_c) + rV(-\Delta H) - \Delta Q\end{aligned} \tag{4.14}$$

where V = reaction volume
F = volumetric flow through reactor
C_{A0}, C_A = concentrations of component A in fresh feed and product
r = rate of reaction
ρ = density
C_{P0}, C_P = heat capacity of feed and product streams
M_w = mass of metal wall in reactor
C_w = heat capacity of metal wall in reactor
T_0, T, T_c = feed, reactor, and jacket temperatures
UA = heat transfer capacity of cooling jacket
ΔH = heat of reaction
ΔQ = reactor heat loss

This model formulation assumes that the reactor wall temperature on the coolant side is the same as the temperature of the reactor contents. The rate of reaction is modeled as

$$r = kC_A = A_f e^{-E_a/RT} C_A \tag{4.15}$$

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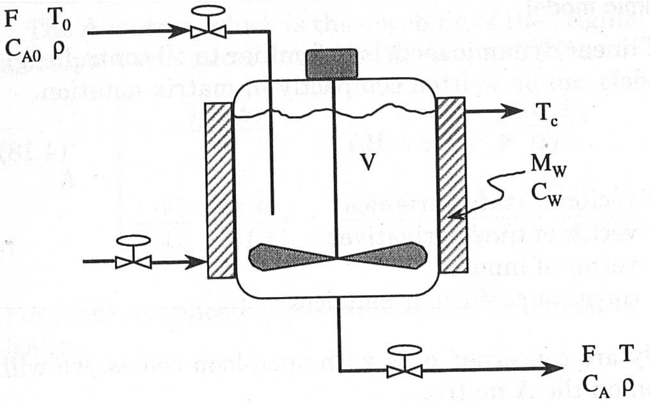


Figure 4.5 CSTR model nomenclature.

Equations (4.13) to (4.15) represent a nonlinear, dynamic reactor model suitable for simulation on a digital computer. From this model we can derive other models that are useful for control explorations of the reactor.

4.4.2 Nonlinear steady-state model

A nonlinear steady-state model is obtained by setting the derivatives equal to zero in Eqs. (4.13) and (4.14). This gives a set of nonlinear algebraic equations that normally have to be solved numerically. However, in this particular case we can find an explicit solution for C_A in terms of temperature.

$$C_A = \frac{C_{A0}}{1 + \tau A_f e^{-E_a/RT}} \qquad (4.16)$$

where $\tau = V/F$ is the residence time of the reactor.

Equation (4.16) is combined with Eqs. (4.15) and (4.14) to produce the following implicit equation in temperature:

$$\frac{\tau A_f e^{-E_a/RT}}{1 + \tau A_f e^{-E_a/RT}} \frac{C_{A0}}{\rho}(-\Delta H) = \left(C_P + \frac{UA}{F\rho}\right) T - C_{P0}T_0 + \frac{\Delta Q - UAT_c}{F\rho} \qquad (4.17)$$

Equations (4.16) and (4.17) are required to explore issues around output multiplicity and steady-state sensitivity.

4.4.3 Linear dynamic model

The usefulness of linear dynamic models is familiar to all control engineers. Linear models can be written compactly in matrix notation.

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} + \mathbf{B}\mathbf{u} \tag{4.18}$$

where $\mathbf{x}$ = vector of state variables
$\dot{\mathbf{x}}$ = vector of time derivatives
$\mathbf{u}$ = vector of inputs
$\mathbf{A}$ and $\mathbf{B}$ = constant coefficient matrices

Since we presently are concerned only with open-loop issues, we will focus our attention on the **A** matrix.

A linear model can be derived from its nonlinear counterpart by linearization. We rearrange the original set of nonlinear differential equations [Eqs. (4.13) to (4.14)] such that the time derivatives are explicit functions of all the states.

$$f_1 = \frac{dC_A}{dt} = \frac{(C_{A0} - C_A)}{\tau} - r \tag{4.19}$$

$$f_2 = \frac{dT}{dt} = \frac{F\rho(C_{P0}T_0 - C_PT) - UA(T - T_c) + rV(-\Delta H) - \Delta Q}{V\rho C_P + M_wC_w} \tag{4.20}$$

The derivatives are then expanded as Taylor series around a steady state. For example, the first few terms of f_1 take the following form:

$$f_1 = \overline{f}_1 + \left(\frac{\partial f_1}{\partial C_A}\right)_T (C_A - \overline{C}_A) + \left(\frac{\partial f_1}{\partial T}\right)_{C_A} (T - \overline{T}) + \cdots \tag{4.21}$$

where the overbar means that the variable is evaluated at steady-state conditions. When we truncate the Taylor series after the linear terms and introduce perturbation variables, $\tilde{C}_A$ and $\tilde{T}$, defined as

$$\tilde{C}_A \equiv C_A - \overline{C}_A$$

$$\tilde{T} \equiv T - \overline{T}$$

we obtain the desired result

$$\begin{pmatrix} \dfrac{d\tilde{C}_A}{dt} \\ \\ \dfrac{d\tilde{T}}{dt} \end{pmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial C_A} & \dfrac{\partial f_1}{\partial T} \\ \\ \dfrac{\partial f_2}{\partial C_A} & \dfrac{\partial f_2}{\partial T} \end{bmatrix} \begin{pmatrix} \tilde{C}_A \\ \\ \tilde{T} \end{pmatrix} \tag{4.22}$$

The **A** matrix, which is the Jacobian of the original equation set, has a compact analytical form for the simple CSTR:

$$\mathbf{A} = \begin{bmatrix} -\dfrac{1+\bar{k}\tau}{\tau} & -\dfrac{\bar{k}\bar{C}_A E_a}{R\bar{T}^2} \\[2ex] \dfrac{V(-\Delta H)\bar{k}}{V\rho C_P + M_w C_w} & \dfrac{-F\rho C_P - UA + \bar{k}\bar{C}_A V(-\Delta H)E_a/R\bar{T}^2}{V\rho C_P + M_w C_w} \end{bmatrix} \tag{4.23}$$

For more complicated systems the Jacobian must be evaluated numerically.

4.5 Open-Loop Behavior

4.5.1 Multiplicity and open-loop instability

No matter how well we design a plant's control system, there will be times when the plant operators feel they need to intervene by switching some controllers into manual and running the process open-loop. When they do that, they certainly expect the process to respond to changes in the valve positions. They also expect that each unit operation will find a unique steady state for a given set of valve loadings. But what if the process can produce different results for the same constant inputs? Or what if the process can start oscillating or run away while the control valves are held in constant positions? This would be most confusing and undesirable. These phenomena, related to output multiplicity and open-loop instability, can occur in chemical reactors if not properly considered during reactor design.

The idea that a unit operation could have two or more steady states for the same values of the input variables is not only confusing in practice but somewhat hard to understand conceptually. We will try to explain the situation, first in words and then graphically. The verbal explanation of multiplicity centers around two of the necessary conditions: nonlinearity and process feedback.

The need for nonlinearity is easy to see. A linear equation has no more than a single solution. A quadratic equation may have two solutions, etc. The describing equations for a reactor must therefore be nonlinear to show output multiplicity.

We next turn to process feedback. We mentioned earlier that a plug-flow reactor can be viewed as a string of small batch reactors. We also pointed out that the result of each batch is uniquely determined by the fresh feeds since the solution to the batch equations is a forward integration in time. A plug-flow reactor cannot by itself show output multiplicity or open-loop instability. This picture changes when we start recycling material from the end of one batch to the beginning of the next. Now, the output is no longer uniquely determined by the fresh feeds but depends, in a sense, on its own value. The ambiguity created by the recycle (process feedback) makes it possible to have more than one solution for the same fixed fresh feed conditions. Since CSTRs have infinite internal recycle ratios they are perfect candidates for output multiplicity and open-loop instabilities.

The graphic illustration of output multiplicity focuses on the steady-state solutions of Eq. (4.17). This equation can be viewed as a trade-off between a nonlinear heat generation term, $Q_{gen}(T)$, and a linear heat removal expression:

$$Q_{rem}(T) = a_1 T - a_0$$

In Fig. 4.6 we have plotted a typical heat generation expression (curve *a*) along with the heat removal line, *b*. In this case the two curves intersect at three locations corresponding to three different reactor conditions that are possible for the same operating parameters and feed conditions. The low-temperature steady state is uneconomical since the feeds are virtually unconverted. The highest-temperature steady state has nearly complete conversion but may be too hot. Under those conditions side reactions may set in or the reactor pressure becomes too high. The middle steady state strikes a good compromise and is where

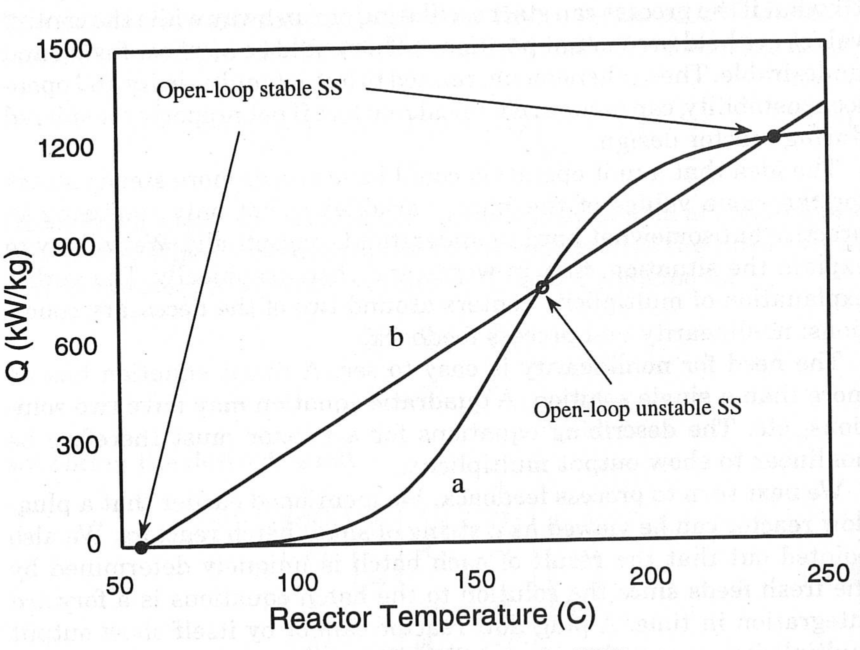


Figure 4.6 Heat generation and heat removal curves for CSTR.

we would like to operate. Will the reactor stay there when the operator switches the reactor temperature controller into manual? The answer is no! The middle steady state is always open-loop unstable when there are three steady states. It is easy to see why. At the middle steady state the heat generation curve has a steeper slope than the heat removal line causing the reactor to drift away from this point. A small increase in temperature, for example, will stimulate more heat production than heat removal and the temperature goes up further yet until the reactor reaches the hottest steady state. Therefore, operation at an open-loop unstable steady state, even if it is feasible with feedback control, is undesirable and should be avoided by proper design of the reactor and its heat exchanger. We refer to the original papers by van Heerden (1953, 1958) and to Arbel et al. (1995b) for further discussions on output multiplicity and unstable steady states in reactors with process feedback.

4.5.2 Open-loop oscillations

How can we change the design of the reactor and its cooling system so that the middle steady-state in Fig. 4.6 is stable? Based on the reason why the middle steady state is unstable we need to increase the slope of the heat removal line beyond that of the heat production curve. This is the so-called slope condition. A quick glance at Eq. (4.17) reveals that the slope condition could be satisfied by providing more heat transfer area in the cooler (increase *UA*). Fortunately this is not hard to do at the design stage. Figure 4.7 shows a design where the slope condition is met such that there is only one intersection between the curves. Surely this single steady-state must be stable? Not necessarily. The slope condition is a necessary condition for stability but it is not sufficient. A complete analysis involves examining the dynamic stability from the linearized system as shown by Bilous and Amundson (1955). They pointed out that the roots γ_1, γ_2 of the open-loop characteristic equation for a two-dimensional system have the following values

$$\gamma_1, \gamma_2 = \frac{-(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})}}{2} \qquad (4.24)$$

where $(-a_{ij})$ is the element in row *i*, column *j* of the Jacobian matrix **A** and γ_i are the eigenvalues of **A**. For a two dimensional system it is clear that the roots will have negative real parts if, and only if,

$$a_{11} + a_{22} > 0$$

$$a_{11}a_{22} - a_{12}a_{21} > 0$$

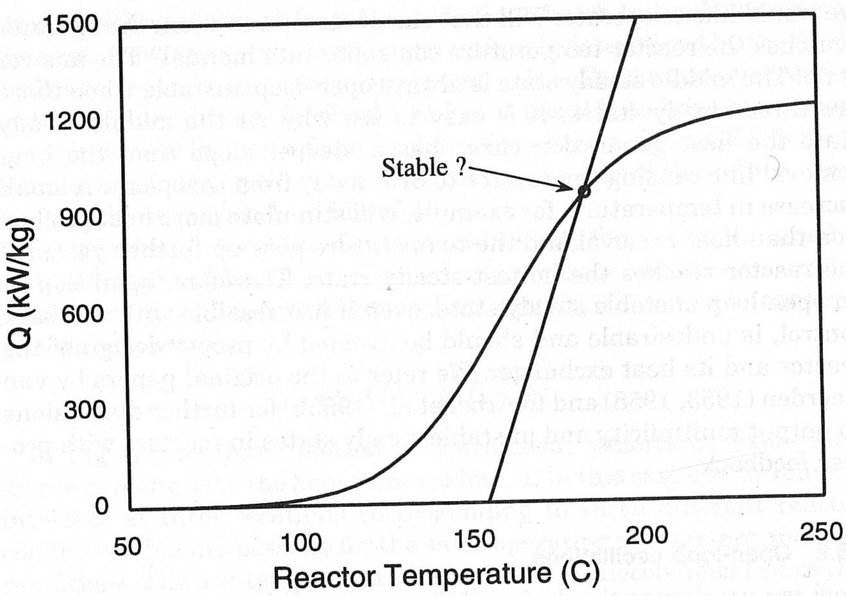


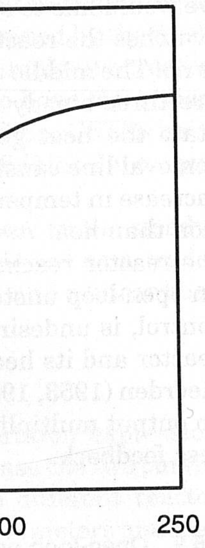
Figure 4.7 Exothermic CSTR with single steady-state condition.

To demonstrate the importance of performing an eigenvalue analysis on a reactor system with backmixing we cite an industrial example reported in a paper by Vleeschhouwer et al. (1992). A schematic of their 6000-L oxidation reactor with heat exchange is shown in Fig. 4.8. The authors claim that a simple CSTR model provides a good representation of the actual system. From the information provided in their paper we plotted the heat generation and removal curves to verify that the slope condition was met (see Fig. 4.7). We next inserted the reactor and operating parameters into Eqs. (4.23) and (4.24) to arrive at the following eigenvalues for the steady state given in the paper.

$$\gamma_1, \gamma_2 = \frac{0.00024 \pm i\sqrt{9.1 \times 10^{-5}}}{2} \tag{4.25}$$

The steady state is evidently dynamically unstable since the eigenvalues have positive real parts. In addition, the eigenvalues are complex, indicating that the system will move away from its unstable steady state in an oscillatory fashion.

Figure 4.9 shows the results of a dynamic simulation we performed featuring the open-loop behavior of a backmixed reactor that satisfies the slope condition for steady-state stability but has dynamically unstable roots. Table 4.1 contains the reactor parameters and operating conditions used in the model, as listed by Vleeschhouwer et al. (1992).



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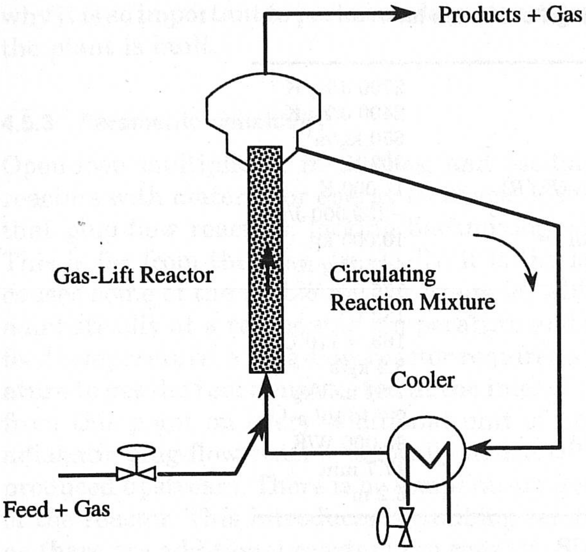

Figure 4.8 Oxidation reactor.

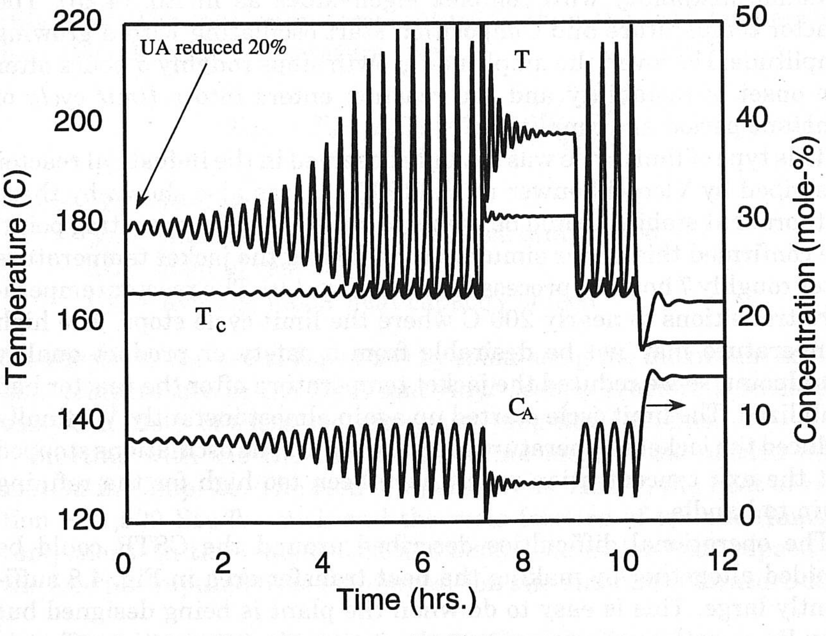

Figure 4.9 Open-loop dynamic response of oxidation reactor.