INTRODUCTION

It should be noted that the coverage of this section and of the previous one (8.9) are similar. If the reader is interested in a detailed and complete treatment of the subject of chemical reactor control, it is recommended to also read that section. On the other hand, if you have little time and you are an experienced process control engineer who is familiar with the basics of chemical reactor control and want only to quickly refresh your memory about the most important aspects of this area of process control and optimization, you should read this section.

OBJECTIVES

The optimization of batch and continuous chemical reactors has many potential benefits, including increase in productivity and improvement in safety, product quality, and batch-to-batch uniformity. Such results are the consequences of many individual control loops and strategies. These loops will maintain material balances, hold optimum temperature and pressure, and control concentrations, while providing safe operating conditions. All elements of the overall chemical reactor control system are discussed in this chapter.

The reactor is the heart of most chemical production facilities. Other operations such as heat transfer, separation, recycle, purification, and drying all are dependent on the reactor’s production and demands for services. Most reactors are “base-loaded,” i.e., their feed rate is fixed, as determined by market demand and constraints. All other operations are then dependent on the reactor’s production rate.

Therefore, it is essential that the reactor operation be stable. If the reactor is run efficiently, with steady product of uniform quality, all other operations may proceed smoothly and the plant should be profitable. But if temperature control is erratic, for example, product quality will suffer and all downstream plant operations will be upset.

Safety

Several objectives must be met for successful reactor operation. The first is always safety. Most chemical reactions in production facilities are exothermic, which means that they produce heat, much like the combustion of fuel. That heat must be removed as it is produced, to maintain a constant temperature. If it is not, the temperature will rise, which increases the rate of reaction, creating the possibility of a thermal runaway—in the extreme case resulting in a fire or explosion. For the protection of life, equipment, and the environment, such an outcome must be prevented. But less extreme conditions can damage product, deactivate catalyst, and foul heat-transfer surfaces—these also must be avoided.

Maximizing Yield

Operating a reactor safely is not enough. It must also operate profitably. This means maximizing yield and minimizing operating costs. Yield is the fractional or percentage salable product that can be made from a given feedstock.

Ideally, 100% of the ethylene fed to an oxidation reactor should be converted to ethylene oxide, but some is invariably converted to carbon dioxide and other by-products of the reaction. If the reaction that produced some of the by-products is reversible, then they may be recycled to reduce their further production and do not represent a loss in yield. But some, like carbon dioxide, will have to be purged from the system and therefore lost.

To maximize yield, it may be necessary to limit conversion, which represents the fraction of the feed that is converted to product on one pass through the reactor. The unconverted feed must be separated from the product and recycled. Operating costs increase with recycling, as it increases the loading on pumps, compressors, and separation equipment. So, there must be a balance struck between yield and conversion, reflecting the cost of lost yield and the operation of the equipment carrying the recycle, along with their constraints.

The Catalyst

Most reactions are catalyzed, as well. A catalyst is a substance that does not change during the reaction, but increases the reaction rate, allowing a higher yield, or higher conversion, or production to take place under less severe conditions of pressure and temperature. Reactions take place on the catalyst surface, so that a large, active surface is essential. Most catalysts are porous, and pore size can affect their
selectivity for particular reactions. Many are inert ceramics coated with active metals like platinum.

The catalyst may be fixed, such as shaped material packed or spaced in a bed. Some catalysts are very fine and fluidized by the upward flow of the reaction mass, as in a fluid cat-cracker, which breaks heavy oil into smaller gasoline molecules. Some catalysts travel with the reaction mass as a slurry, or may even be dissolved. Polymerization reactions usually require an initiator, which is used to create an active site on a molecule, attracting other molecules into a chain reaction.

Catalysts are costly, many having active surfaces of noble metals. While they are not changed by the reaction, they can be degraded, and even poisoned. Degradation consists of clogging the pores or coating the active surface with coke or tar, for example. The fluid cat-cracker contains an auxiliary unit for burning the coke continuously off the catalyst, thereby regenerating its surface and recirculating it to the reactor.

A fixed catalyst bed must be regenerated off-line, which takes time and interferes with production. Some catalysts are poisoned by heavy metals and sulfur, which may require their eventual replacement. Close control of operating conditions can minimize the cost of catalyst loss and regeneration.

CHEMICAL REACTION KINETICS

The conduct of chemical reactions follows an exact science called chemical kinetics, which describes the relationships that produce reactions. The first relationship is one of equilibrium. Most chemical reactions are reversible and terminate in a condition of equilibrium, where forward and reverse rates are equal. As an example, consider the partial oxidation of ethylene to ethylene oxide:

\[
\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4\text{O} + \text{heat}
\]

This equilibrium is defined by an equilibrium constant \(K\), defined as

\[
K = \frac{[\text{C}_2\text{H}_4\text{O}]}{[\text{C}_2\text{H}_4][\text{O}_2]^{1/2}}
\]

where the bracketed terms are molar concentrations of the components. To shift the equilibrium to the right, i.e., to make more product, the concentration of either ethylene or oxygen may be increased, or the concentration of ethylene oxide reduced. The reactant concentrations can be increased by increasing the operating pressure, as they are gases, and the product concentration can be reduced by condensing it to a liquid.

This forward reaction is of 1.5 order, in that it depends on the first power of ethylene concentration and 0.5 power of oxygen concentration; the reverse reaction is first-order. Many reactions are second-order, but most ultimately can be treated as first-order. The reason for this is that favorable conditions for most reactions have one reactant in dominant concentration and the other in a much smaller concentration, the smaller thereby controlling the reaction. At equilibrium, forward and reverse reaction rates are equal, the equilibrium constant being their ratio.

Batch Reactions

In a first-order reaction, the rate of conversion of reactant of concentration \(x\) varies linearly with that concentration and rate coefficient \(k\), expressed in units of inverse time:

\[
-\frac{dx}{dt} = kx
\]

In a batch reactor, that concentration will change with time \(t\), as the rate equation is integrated between initial and final conditions:

\[
\int_{x_0}^{x} \frac{dx}{x} = \int_{0}^{t} -k dt
\]

where \(x_0\) is the initial concentration and \(x\) is its value at time \(t\).

The solution of the above is

\[
x = x_0 e^{-kt}
\]

where \(e\) is 2.718, the base of natural logarithms. The fractional conversion of feed to product in a batch reactor at time \(t\) is

\[
y = \frac{x_0 - x}{x_0} = 1 - e^{-kt}
\]

Continuous Plug-Flow Reactors

Continuous reactors operate with a uniform flow of feed in and product out. The average time spent by a molecule in a continuous reactor is called its residence time and is simply reactor volume \(V\) divided by total volumetric flow \(F\), i.e., \(V/F\). In an ideal plug-flow reactor, ingredients flow from inlet to outlet without any longitudinal mixing. In this way, the ideal plug-flow reactor resembles a batch reactor, in that the fractional distance a molecule travels from inlet to outlet is also its fractional residence time in the reactor. As a result, fractional conversion at the exit of a plug-flow reactor is

\[
y = 1 - e^{-kV/F}
\]

At \(kV/F = 1\), fractional conversion is 0.632. Actual plug-flow reactors may have some longitudinal mixing, but the intent of the design is to avoid it, as back-mixing reduces conversion.
Continuous Back-Mixed Reactors

If a vessel is thoroughly mixed, reactant concentration is the same everywhere, including in the product stream withdrawn. The rate of reaction is therefore determined by the outlet concentration, which is lower than that at any point within the plug-flow reactor. Production rate in a perfectly back-mixed reactor is its volume times the rate of loss of reactant concentration, which is also its feed rate multiplied by the loss in reactant concentration from inlet to outlet.

\[- \frac{Vdx}{dt} = kVx = F(x_0 - x)\]

Solving for exit concentration gives

\[x = \frac{x_0}{1 + kV/F}\]

And fractional conversion is

\[y = 1 - \frac{1}{1 + kV/F}\]

8.10(5)

For the same residence time and rate coefficient, conversion will always be less in the back-mixed than the plug-flow reactor, as shown in Figure 8.10a. At \(kV/F = 1\), fractional conversion is 0.5. However, a back-mixed reactor is lag-dominant and is, therefore, easier to control than the plug-flow reactor, which is dominated by dead time.

Effect of Temperature

Temperature has a profound effect on reaction rate, through an exponential relationship to the rate coefficient:

\[k = ae^{-E/R_T}\]

8.10(6)

where \(a\) and \(E\) are constants particular to the reaction, \(R\) is the universal gas constant, and \(T\) is the absolute temperature of the reaction mass. The nature of the relationship is that reaction rates tend to double with each increase in temperature of about 10°C (18°F). The rate coefficient for a typical reaction normalized to what it would be at 70°C is plotted vs. temperature in Figure 8.10b. This effect is so dominant that precise control of temperature is the most important aspect of operating reactors of any type.

For all reactors, then, conversion is a function of both temperature and time. Because conversion in plug-flow and back-mixed reactors differs as a function of residence time, they can also be expected to differ as a function of temperature.

This is shown in Figure 8.10c, where both reactors are operated at \(kV/F = 1\) at 70°C. Other values of \(V/F\) produce
parallel curves. Because Figure 8.10b shows a doubling of $k$ for about 9°C temperature rise, parallel curves for doubling or halving of $V/F$ will be spaced 9°C apart. For example, the plug-flow reactor will produce 63.2% conversion at 61°C and half the feed rate, and also at 79°C with twice the feed rate.

**EXOTHERMIC REACTOR STABILITY**

Endothermic reactions are inherently self-regulating, because heat must be continuously applied for them to proceed—remove the heat and they die. Ordinary heat transfer is also self-regulating. Increasing the temperature of a hot fluid entering a heat exchanger will increase the rate of heat transferred to the coolant without any change in its flow. Exothermic reactors, by contrast, can be steady-state unstable—depending on their heat-transfer capability—and even uncontrollable. Moreover, some have been observed to change between stable and uncontrollable states.

**Steady-State Stability**

Consider an exothermic reactor operating at steady-state—constant temperature—in the open loop. A small upset causes its temperature to rise, which increases the rate of reaction, thereby releasing more heat. The increase in heat release then raises the temperature further—positive feedback. At the same time, however, the rising temperature increases the rate of heat transfer to the coolant—negative feedback. Which has the stronger influence will determine the steady-state stability of the reactor. Figure 8.10d compares the heat-release and heat-transfer capabilities of a stable exothermic reactor.

In Figure 8.10d, the conversion vs. temperature plot of the plug-flow reactor is equated to heat release by multiplying by the reactant feed rate $F$ and the heat of reaction $H_r$:

$$Q_r = y_x F H_r \quad 8.10(7)$$

Here, it is normalized to 100% conversion at nominal feed conditions. On the same plot is a line representing heat transfer from the reactor to the coolant:

$$Q_t = UA \Delta T_m \quad 8.10(8)$$

where $U$ and $A$ are the heat-transfer coefficient and area respectively, and $\Delta T_m$ is the mean temperature difference between the reactor and the coolant. (If the reactor were a well-mixed vessel and the coolant rapidly circulated past its heat-transfer surface, $\Delta T_m$ could be a simple difference between reactor and coolant temperatures. In practice, this is not likely to be the case, but a mean temperature difference formula can be fitted to whatever heat-transfer configuration exists.) Heat flow in and out of the reactor is set equal at 70°C, the control point.

If the slope of the heat-transfer line exceeds that of the heat-release curve at the operating point, as is the case in Figure 8.10d, the reactor is stable. A rise in temperature transfers more heat than is released, resulting in a stabilizing of temperature. The key to achieving this stability lies therefore in designing the heat-transfer system to have sufficient area for the expected heat load. Area cannot be traded for colder coolant—they are not equivalent as a guarantor of reactor stability. Note that $\Delta T_m$ for the stable reactor in this example is only 16°C.

The slope of the heat-release curve can be determined by differentiating the conversion curve. For the plug-flow reactor, the slope is

$$\frac{dy}{dT} = -\frac{E}{RT^2}(1-y)\ln(1-y) \quad 8.10(9)$$

And for the back-mixed reactor, it is

$$\frac{dy}{dT} = \frac{E}{RT^2}(1-y)y \quad 8.10(10)$$

The maximum slopes of both curves occur where $kV/F = 1$. At that point, the slope of the plug-flow curve is exactly twice that of the back-mixed curve. The plug-flow reactor is therefore twice as demanding of the heat-transfer surface to remain stable.

For pilot-scale reactors, jacket cooling may be sufficient for stability, especially with stirred tanks. However, there is a scale-up problem: Production increases with volume, which increases with the cube of diameter, whereas jacket area increases only with its square. At some scale, jacket cooling is insufficient, and additional heat-transfer surface is required. This can be provided by internal coils, by a reflux condenser, or by an external exchanger through which reactor contents
are circulated. Most full-scale plug-flow reactors have external exchangers.

**Unstable but Controllable**

The heat-transfer surface in Figure 8.10e has been reduced by half from that in Figure 8.10d—increasing $\Delta T_m$ to $32^\circ C$—and now the reactor is steady-state unstable. Any rise in temperature above the control point will release more heat than is transferred, augmenting the rise until the upper stable intersection of the line and the curve is reached. Conversely, any drop in temperature will cause heat release to fall more than heat transfer until the lower stable intersection is reached. In the open loop, the temperature will seek one of the two stable intersections, running away from the desired control point.

A simple model of the unstable reactor is the inverted pendulum—a stick balanced vertically in the hand, for example. Its balanced position is an unstable steady state, in that the slightest disturbance will cause it to accelerate away from that state. However, it is possible for a person, or even a trained seal, to balance a stick for a time. To be successful in doing so reveals the control effort required. As soon as the stick begins to deviate from a true vertical position, the hand must move farther in the same direction to restore balance. In other words, the gain of the (human) controller must exceed unity to succeed in controlling a steady-state-unstable process.

That is, the process is controllable if the gain of the controller can be set high enough. Reference 1 identifies the limit of controllability of the steady-state-unstable process as when the dead time in the loop approaches its time constant. In other words, a lag-dominant unstable reactor is controllable, whereas a dead time-dominant one is not.

A stirred tank is more likely to be stable than a plug-flow reactor, because the maximum slope of its heat-release curve is only half as great. But even if unstable, it is controllable because it is dominated by the large lag of its well-mixed contents. To be sure, its control loops need to be properly structured, a subject to be covered. But the proportional gain of a typical temperature controller on a back-mixed reactor is in the order of 3:5, which is entirely capable of controlling it even if it is unstable.

**Uncontrollable Reactors**

Plug-flow reactors are dominated by dead time and, if unstable, are therefore also uncontrollable. During start-up, as temperature is raised, they may behave well because reaction rate is low at the lower temperatures. But as the desired operating temperature is approached, there is a tendency for the reactor to speed right past it. Even a carefully structured control system will not be able to stop it in time. As the temperature rises further, the slope of the heat-release curve moderates, and the manipulated cooling begins to bring the temperature down. But it then goes past the control point in a downward direction, until the control system arrests the fall.

The result is a limit-cycling of the temperature—at a given set of conditions, the cycle will be of uniform amplitude and period and nonsinusoidal, possibly sawtooth in shape. Its amplitude will depend on the difference between the slopes of the heat-release curve and the heat-transfer line at the control point.

One of the characteristics of a limit cycle is its resistance to change. Variations in the tuning of the temperature controller(s) tend to have little effect—itss period and amplitude may change slightly, but the cycle persists. The only way to stop the temperature from cycling is to lower the production rate, which reduces the slope of the heat-release curve, or to improve the heat-transfer condition. A reactor that was once controllable and is no longer, may be suffering from a fouled heat-transfer surface—cleaning has been observed to restore stability.

**TEMPERATURE CONTROL**

Unless reactor temperature can be controlled precisely, product quality will vary. This is especially true of polymerization reactions, where molecular weight, density, and viscosity are all functions of reactor temperature. Variations as small as $1^\circ C$ may produce unsatisfactory product.

**Measuring Temperature**

Resistance-bulb sensors are universally used to measure reactor temperature, as they are more accurate than thermocouples. In a well-stirred tank, the measurement may be made anywhere within the mixed zone, velocity being necessary for dynamic response and to avoid fouling. The sensor must
be protected against corrosion and erosion, requiring installation in a well in most cases—then close thermal contact of the sensor with the well is necessary to maximize dynamic response.

The temperature will vary along the length of a plug-flow reactor, due to the variable rate of reaction within. In an adiabatic reactor (no heat removal), temperature will rise throughout. For one that is cooled by a jacket, a peak temperature will usually be reached along the first third of travel from the inlet.

In a packed bed, that hot spot may move downstream gradually as catalyst decays. There may also be a radial gradient. Therefore, most plug-flow reactors have multiple sensors, one of which may be manually selected as the control point. Selection may even be automatic, as the highest of several measurements. An average of two or more temperatures may also be used for control, or the median of three or five measurements, as being more representative of the reaction mass. However, if the combined sensors are spaced too far apart, a difference in their dynamic responses may require the controller settings to be compromised.

Reactor pressure, or rather its change, has been used to predict reactor temperature change. The rationale is that pressure changes directly with temperature, but faster, because it lacks the lags in the bulb and thermowell. However, the steady-state value of pressure is misleading, because it is too easily influenced by variations in composition, particularly the presence of noncondensable gas.

Therefore, the predicted temperature is best calculated as the measured temperature plus a gain factor times the rate of change of pressure. This method was tried by the author on an uncontrollable reactor, but unsuccessfully. The predicted temperature led the measured temperature when falling, but not when rising, and so was ineffective in stabilizing the loop. It was only a half-predictor.

**Manipulating Coolant Flow**

It is possible to control the temperature of a continuous reactor by manipulating feed rate at a constant coolant flow—but it is also very dangerous! If the reaction mass is cold, reaction rate and heat release will be low, and adding more feed will not raise the temperature. Under these conditions, it is possible to overheat a reactor, so that when reaction temperature is reached, there will not be enough cooling available to remove the heat released, resulting in a thermal runaway. But even beginning at a steady state, manipulating feed rate is poor practice.

A change in feed rate must first change reactant concentration through the concentration lag, and then change temperature through the thermal lag. These are two large lags in series. The concentration time constant is

$$\tau_c = \frac{1}{k + F/N} \quad 8.10(11)$$

and the thermal time constant is

$$\tau_T = \frac{MC}{UA} \quad 8.10(12)$$

where $M$ and $C$ are the reaction mass and specific heat, respectively. There is also the problem of inverse response: Increasing the flow of cold feed will cause the temperature of the reaction mass to fall before the effect of the increased concentration of the reactant causes it to rise. This reversal could last for several minutes, resulting in very unfavorable dynamic response. This scheme is not recommended to control an exothermic reactor.

Manipulating the flow of coolant is necessary for successful temperature control. If it can be injected directly into the reaction mass, then the lags associated with heat transfer are avoided. If not, then a boiling coolant is the best heat sink, as it is isothermal, but such a fluid may not be available or safe or economical in the temperature range desired. Boiling part of the reaction mass and condensing it in a reflux condenser is another self-regulating means of heat removal. However, the most common coolant used for exothermic reactors is water flowing past a heat-transfer surface.

**Tempering Loops**

Manipulating coolant flow in a single pass by the heat-transfer surface is not good practice. Consider, for example, the jacketed batch reactor shown in the previous section in Figure 8.9, whose cooling load varies with time. When little coolant is required, its low flow through the jacket creates a long dead time—catalyst volume divided by the low flow. At higher demands, this dead time decreases. The temperature controller cannot be optimally tuned for all of the possible flowing...
conditions, and must favor the worst case of low flow, giving less-effective control during the major portion of the reaction.

This dead time varying with flow also creates a limit-cycling condition in the temperature loop. A rising temperature causes the controller to increase coolant flow, which decreases jacket dead time and thereby drops temperature quickly. But a falling temperature causes the controller to decrease coolant flow, which increases dead time and delays temperature response.

A temperature cycle is created that then has sharp peaks and flat valleys, and tuning may not be able to remove it. As the cooling load increases, higher flow rates tend to decrease the period and amplitude of the cycle, and it may even disappear at the highest rates.

This behavior can be avoided entirely by the use of a circulating pump on the coolant, as shown in the previous section in Figure 8.9g. Adding coolant lowers the temperature of the jacket contents without affecting internal velocities. The coolant enters the jacket at constant flow and variable temperature, instead of constant temperature and variable flow.

**Valve Selection**

The rate of heat transfer is not linear with coolant flow. Consider, for example, a batch reactor controlled at 70°C by cooling water supplied at 20°C. If there is no cooling load, then the coolant in the circulating loop will be at the same temperature as the reactor, with no fresh coolant added. Opening the coolant valve will add water at the supply temperature of 20°C while displacing water at 70°C—each increment of water carries away heat proportional to that 50°C of temperature rise. However, at full heat load, the coolant exit temperature will be much lower, possibly as low as 30°C. Now the same change in water added removes heat proportional to a temperature rise of only 10°C.

The gain in converting coolant flow to heat transfer varies by 5:1 between zero and full load.

When a logarithmic-mean temperature difference is used to relate heat transfer to coolant temperatures in a jacketed stirred tank, the ratio of fresh coolant mass flow \( W_C \) to circulating flow \( W \) is derived as a hyperbolic function of heat load:

\[
\frac{W_c}{W} = \frac{1}{WC_c(T_r - T_c)\frac{\Delta Q}{W} - \ln(\varepsilon - 1)}
\]

where \( C_c \) is the specific heat of the coolant, and

\[
\varepsilon = e^{UA/WC_c} = \frac{T_r - T_{C1}}{T_r - T_{C2}}.
\]

Temperatures \( T_{C1} \) and \( T_{C2} \) are those of the circulating coolant entering and leaving the jacket, respectively, at any given steady state; if \( U, A, \) and \( W \) are constant, \( \varepsilon \) is also constant.

This relationship is plotted for the reactor described above as the numbered curves in Figure 8.10f, for a range of coolant flow up to half the circulated flow, and two values of \( \varepsilon \). \( \varepsilon = 1.125 \) corresponds to jacket inlet and outlet temperatures of 25 and 30°C, and 1.333 corresponds to jacket inlet and outlet temperatures of 30 and 40°C at full heat load. The latter case represents a value of \( UA/WC_c \) that is 23% higher. Linear and equal-percentage valve characteristics are plotted for comparison, with the rangeability of the equal-percentage valve being 50:1. The latter matches the required characteristic for \( \varepsilon = 1.125 \) almost perfectly. Matching the process curve by the valve means that heat flow will be linear with valve stroke, and therefore so should temperature.

However, the curve for \( \varepsilon = 1.333 \) shows that such a close match of valve characteristic to the heat-transfer process is not always attained. In fact, Reference 2 describes a gas-phase plug-flow reactor cooled by recirculation of gas through a counterflow cooler, where the process curve is closer to that of \( \varepsilon = 1.333 \). The equal-percentage valve is still the preferred choice, because its variable gain compensates the loop for the effect of changes in coolant supply temperature and reactor temperature set point.

Equation 8.10(13) shows that the relationship between coolant flow \( W_c \) and heat transfer \( Q \) is affected by the temperature difference \( (T_r - T_c) \) as a gain factor. A lower temperature difference decreases the process gain \( dQ/dW_c \) and requires a higher coolant flow for the same level of heat transfer. But the gain of an equal-percentage valve increases directly with flow delivered, thereby compensating for the process-gain change.

**Cascade Control**

Cascade control is recommended for critical variables that are difficult to control and subject to several disturbances, and the temperature of an exothermic reactor certainly fits this case. Cascade control is possible whenever the process can be divided into separate dynamic pieces by the measurement of an appropriate secondary variable. In the case of an exothermic reactor, the two pieces are the reactor itself and its cooling system, and the secondary variable is the temperature of the coolant as it enters or exits the heat-transfer surface.

As shown in Figure 8.9l in the previous section, the secondary or slave loop is closed by a temperature controller whose set point is adjusted by the primary or master temperature controller. The primary controller sees the secondary closed loop and the reactor in series. It is imperative that the secondary loop be faster than the primary, and yet it should contain significant dynamics and disturbance variables to be effective.

The periods of the two loops should differ by a factor of 4 or more to avoid resonance. For the stirred tank, controlling
the jacket outlet temperature closes the loop around the jacket, thus speeding the response of the primary loop and preventing cooling-system disturbances from upsetting the reactor. But plug-flow reactors are faster, and controlling coolant inlet temperature as the secondary variable gives the two loops better dynamic separation.  

Batch exothermic reactors require heating as well as cooling, both for startup purposes and to cure the product and drive off solvent at the end of the reaction. The secondary controller therefore opens cooling and heating valves in split range. The split-ranging is usually accomplished with valve positioners as shown in the previous section in Figure 8.9m, calibrated to open the heating valve from 50 to 100% of the controller output, and the cooling valve from 50 to 0% (the cooling valve fails open).

Because of the difficulty of controlling exothermic reactors and of the critical role played by valves, smart digital positioners are recommended. ² They eliminate stiction and dead band, and maximize response speed. Each valve positioner closes a loop around its valve and therefore constitutes a second level of cascade control, as was shown in Figure 8.9m.

With the provision of heating, additional precautions are advised. A high limit should be set on coolant temperature as shown, and for glass-lined reactors, the temperature difference between the reactor and jacket should be limited to avoid excessive thermal stress. Some polymerization reactors are also fitted with interlocks that prevent heating after the initiator has been introduced into the reactor.

In some polyvinyl-chloride (PVC) processes, the reaction mass is heated to about 70°C without any initiator, and allowed to stabilize at that temperature without any reaction taking place. Then initiator is injected, and the heating valve locked out for safety. A rising temperature then signals the beginning of the reaction. The temperature controllers respond by opening the cooling valve, and after a peak deviation of 2–3°C is reached, the temperature returns toward set point, and in fact, overshoots.

At this point, the secondary controller output rises above 50%, but the heating valve is locked out, so that the secondary loop is open. The temperature slowly begins to rise again, but during the open-loop condition, the primary controller has been winding up—it has raised the set point of the secondary controller, which was unable to respond because of the interlock. As a result, the secondary set point is too high, causing the primary temperature to rise past its set point again. The scenario then repeats, settling into a limit cycle of ±1°C or thereabouts, which does not respond to tuning changes and adversely affects product quality.

The limit cycling is avoided through the use of external reset (ER) from the secondary temperature measurement to the integral-feedback port of the primary controller, as was shown in Figure 8.9m. As long as the secondary temperature is at its set point, the ER signal and the primary controller output are identical, allowing the primary controller to integrate normally. But when the secondary is prevented from controlling (by the locked-out valve, or any other obstacle such as a set-point limit), primary integration stops. The secondary controller must have integral action for this strategy to be successful, because any secondary-loop offset will cause a proportional primary-loop offset.

This feature successfully eliminated limit-cycling in the PVC reactors with the locked-out heating valve. It was also used on batch reactors for latex paint and found to be very robust. In trials, the primary time constant of the reactor was varied over a range of 4:1 by changing batch size and heat-transfer area, each by a factor of 2:1—yet the control system did not require any tuning adjustments. The rate of temperature change was obviously affected by these process conditions, but the dynamic response of the secondary temperature altered the rate of integration of the primary controller sufficiently to accommodate them.

The secondary controller in a cascade system must be tuned before the primary, as it is a part of the primary loop. It should be tuned for optimum load response—not set-point response—regardless of having to respond to its set point. The set-point changes that it sees are gradual, not stepwise, and therefore affect the loop dynamically much the same as load changes do. For the same reason, filtering should never be applied to the secondary set point, and the set point should receive full proportional action (some controllers have the option of eliminating proportional action to the set point). Otherwise, the secondary control action will effectively lag the primary output, negating the dynamic benefit of cascade control.

**Batch Reactor Start-Up**

The problem of integral windup is particularly troublesome during start-up of a batch reactor. The goal is to raise reactor temperature from its initial value (possibly ambient) to an elevated set point (where the reaction proceeds) as quickly as possible, but without overshoot. In this situation, a conventional PID controller will invariably overshoot set point.

Following a large set-point change, its output will saturate, and during the rise time, the integral mode will also saturate. The result is that the output remains at its high limit until the set point is crossed. If the new steady state requires no heating or cooling in absence of a reaction, the new steady-state value of the controller output should be 50%; if an exothermic reaction has begun, the new output should be even lower. As a result, there will be an unacceptable temperature overshoot, such as that shown in the top curve in Figure 8.10g.

Integral windup in the start-up of a batch process can be overcome by the circuit, which was shown in the previous section in Figure 8.9x. The output of the controller is compared with a high-limit setting, and their difference sent to a high-gain amplifier, whose function is to control the controller output at that limit by manipulating the integral feedback term.

If the controller output is below the high limit (say 100%), that output is selected by the low-signal selector (<)
as integral feedback, allowing the controller to integrate normally. If the output moves above the limit setting, the amplifier will manipulate the integral feedback term as needed to hold it at the limit. However, the feedback term can only be reduced to the point where the preload setting is selected by the high-signal selector (>); preload is adjustable to match the expected load when the new steady state is reached.

Overshoot is caused by the integral term staying at the high output limit until set point is reached. Reducing that term to match the expected load—the controller output required to hold temperature at set point in the new steady state—should eliminate the overshoot, and it does.

Without preloading the controller, however, undershoot will result, as shown in the lowest curve in Figure 8.9g. These curves were produced by an interacting PID controller having derivative action on the measurement (derivative was not shown in Figure 8.9x), which also assists in limiting overshoot. If derivative is not used, then the preload setting will have to be reduced somewhat below the expected load, because integration begins as soon as the controller output leaves its limit, which is well before the set point is crossed.

Another method of avoiding overshoot while minimizing start-up time has been used successfully on polystyrene reactors—the dual-mode control system. It consists of an on/off controller for start-up and a PID controller to take over at the new set point, as was schematically depicted in the previous section in Figure 8.9z.

The on/off controller applies full heat until the temperature has almost reached set point—it then switches to full cooling. After a set time delay, control is transferred to a preloaded PID. Switching from full heat to full cooling takes place within 2–3°C of set point, and the time delay is long enough to replace the hot water in the jacket with cold.

The sequence of operation is as follows:

1. Initial conditions have both switches in the A position. Full heat (100% output) is applied by the on/off controller until the deviation falls to the set point of \( E_m \).
2. The on/off controller output then drops to zero, producing full cooling. It also starts two time-delay relays: TD-1 and TD-2.
3. When TD-1 times out, the period of full cooling terminates, and the system output is switched by SS-1 to the preloaded PID controller, without integration.
4. When TD-2 times out, the temperature should be settled at set point. It then transfers switch SS-2 to the B position, enabling integration.

While this system is capable of minimizing start-up time, it is not foolproof. It has three settings more than the batch controller: \( E_m \), TD-1, and TD-2. Furthermore, these settings need to be changed with process conditions such as batch size and reactivity, temperature set point, and heat-transfer coefficient, the last typically decreasing with the number of batches produced, as surfaces foul.

Efforts to adapt these parameters to changing conditions, or to program them with each recipe, have met with limited success. The preloaded batch PID controller with external reset feedback from secondary temperature is much simpler, more universally applicable, and more robust under changing conditions.
MATERIAL BALANCE CONTROL

Most chemical reactions require the precise matching of two reactants to produce a product. One of the challenges of process design is to ensure that all of each reactant is converted to product, regardless of the fractional conversion in the reactor.

A simple example is the neutralization of acid and base—their individual concentrations in solution must be typically matched within ±0.01% for the solution to fall within the pH range of 6–8. A pH sensor is sensitive enough to detect such a minute imbalance, but on-line analyzers are not always available and even when they are, end-point control can be difficult, both in a batch and in a continuous plant.

Even when there is but a single reactant, as a monomer being polymerized, end-point control is necessary to terminate the reaction at the desired chain length or molecular weight or density.

Stoichiometry

_Stoichiometry_ is the term used to describe the balancing of a chemical reaction so that all of the reactants are converted to the desired product. A typical example is the oxidation of hydrogen sulfide to elemental sulfur, which is condensed:

\[ \text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S} \downarrow \]

A simple enough reaction, but if too much oxygen is fed, it will oxidize sulfur to sulfur dioxide in a consecutive reaction:

\[ \text{S} + \text{O}_2 \rightarrow \text{SO}_2 \]

Simply metering the gas and air is not accurate enough, and the H\(_2\)S content of the gas is also usually variable. The key to controlling this reaction is establishing an equilibrium between H\(_2\)S and SO\(_2\) in the tail gas leaving the reactor:

\[ \text{H}_2\text{S} + \frac{1}{2}\text{SO}_2 \rightleftharpoons \frac{1}{2}\text{S} + \text{H}_2\text{O} \]

At equilibrium, where the reaction stops, H\(_2\)S has twice the concentration as SO\(_2\) in the gas phase, and Reference 4 demonstrates that this ratio results in the minimum sulfur loss.

So an analyzer on the tail gas reports both concentrations, and a ratio controller manipulates the air-to-gas flow ratio to hold the H\(_2\)S/SO\(_2\) ratio in the tail gas at a value of 2.0. The system is shown in Figure 8.10h. There is no fixed or set value for either H\(_2\)S or SO\(_2\); they float with production rate and other conditions, but are always at a minimum as long as their ratio is maintained at 2:1. (Note that control of the ratio is achieved without the use of a divider—placing a divider in a closed loop is inadvisable, because its gain varies with the value of the denominator.)

FIG. 8.10h
_Minimum sulfur is lost when the ratio of H\(_2\)S to SO\(_2\) in the tail gas is controlled precisely at 2:1._

Controlling Inventory

When one of the reactants differs in phase from the product(s) and other reactants, its inventory is measurable independently from the others, and it can be fed at the rate at which it is consumed. Two examples were shown in Figure 8.9ii.

A gaseous reactant forming a gaseous product in a liquid-phase reactor will consume the liquid reactant at the rate of reaction. Loss of liquid inventory is sensed by the level, which can be controlled to keep inventory constant. The manipulated flow of liquid feed then directly indicates reaction rate. Because no liquid product leaves the reactor, however, liquid or solid contaminants could accumulate at low points. There should be a liquid purge, either continuous or periodic—just like boiler blowdown—to eliminate the problem. Most plants have facilities for recovering feedstocks and by-products from purge streams—some are only operated periodically, as waste inventory builds.

Similarly, if the product(s) leave in the liquid phase, consumption of a gaseous reactant lowers pressure, indicating a loss in its inventory. A pressure controller can add gaseous reactant as it is consumed. In this case, a small gas purge is required to eliminate inerts such as nitrogen or carbon dioxide. Molecular sieves are often used to recover valuable gases from purge streams.

When feeds and products are in the same phase, inventory control is more difficult. For example, isobutane reacts with butylenes in a 1:1 ratio to produce high-octane gasoline called alkylate, but they are fed to the reactor in a 10:1 ratio to minimize formation of butylene polymers. The process therefore contains a large inventory of liquid isobutane, which must be controlled as it is consumed.

The reactor effluent, containing isobutane, alkylate, and inerts such as normal-butane, must be separated by distillation, with the isobutane being recycled. The recycle storage tank provides an outflow that is 10 times the rate of consumption and make-up of isobutane, and so its time constant is large compared to that of typical liquid-level loops. Proportional-only level control is recommended to allow the tank to absorb variations in production rate without the oscillations that integral action brings to slow level loops.
A similar refining process is the hydrocracking of heavy oil into gasoline fractions. Hydrogen and oil are heated and fed into a series of packed-bed reactors, where partial conversion takes place. Lighter products in the effluent are then removed by distillation, with the unreacted oil recycled under flow control from the column base to the reactors.

The oil is eventually all consumed, but at a rate that varies with temperatures and so on. Its inventory is sensed as the liquid level in the base of the distillation column, and that level controller is used to add more oil. It has also been used to set reactor temperature to convert a fixed flow of oil, but this is more difficult dynamically, as it places a temperature loop within a level loop.

**Reactor Dynamics**

Closing the composition loop on a reactor can be difficult, depending on the reactor dynamics. Ideally, a plug-flow reactor is pure dead time In fact, static mixer elements are often used in a plug-flow reactor to maximize radial mixing and minimize longitudinal mixing. Actually, however, the step response will appear more like a series of noninteracting lags, between 20 and 50 in number, as shown in Figure 8.10i. This would be equivalent to 20–50 ideal back-mixed reactors in series. The response does approach dead time, with 50% completion reached when the elapsed time is equal to the residence time, \( V/F \). It also should be noted that the effective dead time is variable with flow, although large variations are not expected in production reactors.

Ideally, a back-mixed reactor is a pure first-order lag. But perfect mixing is unattainable, and therefore the actual step response reveals a small amount of dead time, dominated by a first-order lag. The sum of the dead time and time constant is the residence time, \( V/F \)—at that point, the response curve crosses 63.2% complete, just as does a single lag.

The back-mixed reactor curve in Figure 8.10i was simulated by 20 interacting lags, although increasing the number above 20 does not change the shape of the curve. It is essentially a distributed lag that is an accurate representation of a heat exchanger, where heat capacity and heat-transfer surfaces are distributed throughout the exchanger.

Reactor composition loops are ordinarily self-regulating, their step response approaching a final steady state as the figure shows. However, many reactors are enclosed in recycle loops that bring positive feedback into the process and eliminate their inherent self-regulation.

Consider, for example, an acid-base reaction carried out in an organic solvent. At the reactor exit, gaseous product is withdrawn, but any excess acid or base remains in the solvent and is ultimately recycled to the reactor. So if \( z \) concentration of excess base remains in the solvent, and the acid-base ratio is not adjusted to allow for its presence in the recycle stream, the concentration will increase to \( 2z \) the next time around, and continue to accumulate.

The integrating time of this recycle loop is the residence time of the solvent in the system—the time required to circulate the entire solvent inventory through the reactor. The significance of this loss of self-regulation cannot be understated. End-point control must be applied, or the composition of the reactor effluent will never reach a steady state. And integral-only control cannot be used to close the loop, or the composition will cycle endlessly—proportional action is essential for stability.

**Batch End-Point Control**

There are two basic types of batch reactors: pure-batch and fed-batch. A pure-batch reactor has all of its ingredients charged at once, and the reaction is allowed to proceed over time until complete. In a fed-batch reactor, one or more of the ingredients is left out of the charge and then fed at a controlled rate over time until the reaction is complete. In both cases, some determination must be made of the reaction's approach to completion, to avoid wasting both chemicals and time.

Polymerization converts light hydrocarbons into high-molecular-weight products having low vapor pressure. They are often conducted as pure-batch processes, with the initial charge under pressure. At reaction temperature, initially the pressure is close to the vapor pressure of the monomer. As the last of the monomer is consumed, the pressure starts falling, indicating completion of the reaction.

Another indication is the decline in heat evolution as the last of the reactant is consumed. Still another is the total quantity of heat transferred to the coolant, which must be determined by calculation and integration. Others measure or infer density or viscosity of the product to determine completion.

Fed-batch processes require termination of feed at the end point, to avoid loss of reactant. This can be done simply by stopping feed when a desired total is delivered, but this may not be accurate enough in some cases. The use of end-point analyzers is recommended, where available. A case in point is the control of pH in a batch of wastewater from a

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**FIG. 8.10i**

The plug-flow reactor is simulated by 20–50 noninteracting lags, the back-mixed-reactor by 20 interacting lags.
small processing plant—it must meet environmental specifications before discharge is allowed.

This is not a typical composition loop requiring a PID controller, because a batch process has no flow leaving it—it is essentially a no-load process. Integral action is needed to eliminate offset whenever a controller must move its steady-state output to match the current plant load. But when the load is zero and stays there, integral action is unnecessary and, in fact, causes irrecoverable overshoot.

Consider a tank filled with impounded industrial wastewater at pH 3—its pH must be raised to 6 prior to discharge, and so 6 is the set point of the pH controller. The large initial deviation of 3 pH will drive the caustic valve fully open, and it will remain open as long as necessary to neutralize the waste. During this time interval, if the integral mode is active it will wind up to the controller output limit, and the output will not fall below that limit until the pH crosses set point. That is clearly too late, and by the time the caustic valve closes, the pH will have risen well beyond set point—perhaps to 9 or 10.

In a continuous plant, overshoot is temporary, because its outflow will eventually purge away excess reagent. But not in a batch plant—the overdose is permanent. The batch will require re-treating with acid or more wastewater to lower the pH.

Because the load is zero, the controller output should also be zero when the controlled variable is at set point. This is achievable by elimination of integral action, replacing it with an output bias of zero—the controller must be proportional-only or proportional-plus-derivative. This is not simply a matter of shutting off integration, as this leaves the constant of integration in place of an output bias, and it floats, changing every time the controller is transferred from manual to automatic. The bias must be a hard, permanent zero, and some controllers—of the incremental or velocity type—do not have this capability. If a pure proportional controller is unavailable, build one out of a calculation block, as follows:

\[ m = K_c (r - c) \]

where \( m \) is the controller output, \( K_c \) its proportional gain, \( r \) the set point, and \( c \) the controlled variable. If derivative action is desired—usually helpful in a composition loop—a leadlag function can be applied to the controlled variable before it enters the controller.

It is possible to feed two reactants simultaneously into a batch reactor with no outflow. The control problem is like trying to fill a bathtub in minimum time. To reach the right temperature at the desired volume, it really needs to be controlled throughout the filling process. This requires finding the flow ratio that produces approximately the right temperature at the start of the filling process, and adjusting it as necessary until the final volume is reached.

Initially, changing the ratio produces a large temperature change, but as the tub fills, this gain gradually decreases. In fact, the dynamic gain of the process varies inversely with the volume of the fill. To effectively control the composition of the variable-volume batch, the gain of the composition controller needs to be changed in direct proportion to the liquid level in the reactor.

REACTOR OPTIMIZATION

After satisfactorily controlling reactor temperature, material balance, and end-point, at the necessary production rate, optimization may be attempted. Optimization generally means maximizing economic return on the plant capital and operating costs, but there are many aspects of this, because there are many cost factors.

In an unlimited market, maximizing production maximizes return on both capital and labor. When the market is limited, meeting production goals with a minimum cost of utilities is essential. Maintenance is also costly, and operating a plant in a way that minimizes cleaning and wear has its savings.

Maximizing Production

Production rate from a reactor is determined by the rate coefficient and residence time. To increase flow rates through a reactor of fixed volume reduces residence time and conversion per-pass, and therefore does not result in a proportional increase in production. The production rate of a first-order reaction is

\[ P = x_y F_y \]

Increasing production by raising the feed concentration \( x_0 \) of the controlling reactant is not often an option, in that it tends to reduce yield, through side reactions and consecutive reactions. In the case of isobutane alkylation, for example, increasing the ratio of butylenes to isobutane above 1:10 increases the formation of polymers having undesirable properties as motor fuel, and consumes more catalyst.

Increasing production by raising feed rate is viable, but inefficient. To determine the effect of feed rate on production it is necessary to differentiate \( F_y \) as a function of \( F \). For the plug-flow reactor,

\[ \frac{d(F_y)}{dF} = y + (1 - y) \ln(1 - y) \]

And for the back-mixed reactor,

\[ \frac{d(F_y)}{dF} = y^2 \]

For the plug-flow reactor operating at \( kV/F = 1 \), \( d(F_y)/dF = 0.264 \), and for the back-mixed reactor it is 0.250. Therefore, increasing feed rate by 1% increases production only...
To increase production without this penalty requires increasing reaction temperature along with feed rate, following the reaction-rate coefficient curve. Only small changes are required, given the rate coefficient doubling approximately every 10°C. In the region around 1.0 in Figure 8.10b, the normalized rate coefficient increases about 10% for each 1°C.

Maximizing production in a back-mixed exothermic reactor amounts to operating at the cooling constraints. Figure 8.9dd described how this is done when manipulating feed rate(s) to a continuous reactor. The position of the coolant valve is sent to an optimizing controller (OIC), which adjusts the feed rate(s) to drive the valve to about 90% open. In other applications, such a valve-position controller would have only the integral mode, but for an exothermic reactor, all three PID modes are necessary for stable operation.

In addition, if a large difference develops between the positions of the feed and coolant valves—or more accurately between feed and heat-transfer rates—this is an indication that the reaction is not proceeding normally and should be shut down before excessive amounts of reactant(s) have been fed. The OIC loop must be slower than the temperature loop that is inside it, and great care must be taken in closing it. The OIC loop arose out of operators’ practice of observing the steady-state position of the coolant valve and gradually increasing the feed to a fed-batch reactor to drive the valve almost fully open. The same operators respected the conditions under which this could be done safely, namely that the reactor had been properly charged and initiated, and was already at the controlled temperature.

There is no feed rate to manipulate in a pure-batch reactor. Furthermore, the reaction rate tends to vary as reactants are consumed. To minimize run time then requires the OIC to adjust the temperature set point to drive the coolant valve to 90% open. This is a difficult loop, however, exhibiting inverse response. To open the coolant valve further requires increasing temperature set point. However, when its set point is increased, the temperature controller responds by closing the coolant valve first. As the temperature then begins to rise, the controller will eventually open the coolant valve more than before, but this takes time. Again, the OIC requires full PID control, and must be much slower than the reactor temperature controller.

Maximizing production based on the position of the coolant valve is not always applicable on plug-flow reactors. If the coolant valve is obviously limiting production, as can happen during peak summer weather, then it may work. However, Reference 2 describes an uncontrollable reactor limit-cycling in winter, when the equal-percentage coolant valve was only 10–20% open.

Production rate was limited by the heat-transfer surface of the cooler and not by the coolant valve or supply temperature. The maximum controllable production rate of a plug-flow reactor is determined by the slope of the heat-transfer line in Figure 8.10d. At the limit of stability, the slopes of the heat-release and heat-transfer curves are the same. The slope of the heat-release curve is

$$\frac{dQ}{dT_r} = x_r F H_r \frac{dy}{dT_r}$$

8.10(17)

and that of the heat-transfer curve is $UA$. Therefore, the maximum controllable feed rate is

$$F_{max} = \frac{UA}{x_r H_r (dy/dT_r)}$$

8.10(18)

To monitor $UA$ requires the calculation of the logarithmic-mean temperature difference across the cooler:

$$UA = \frac{Q}{\Delta T_m}$$

8.10(19)

where for counter-current heat transfer,

$$\Delta T_m = \frac{(T_{H1} - T_{H2}) - (T_{C1} - T_{C2})}{\ln \left(\frac{T_{H1} - T_{C2}}{T_{H2} - T_{C1}}\right)}$$

8.10(20)

$Q_t$ may be calculated either from fresh or circulated coolant flow:

$$Q_t = W C C (T_{C2} - T_{C1}) = W C C (T_{C2} - T_{C1})$$

8.10(21)

$T_{H1}$ and $T_{H2}$ are temperatures of the reaction mass entering and leaving the heat-transfer surface, respectively.

For a plug-flow reactor prone to fouling, $UA$ or $\Delta T_m$ should be monitored regularly and compared to production schedules. In this way, cleaning can be scheduled in advance, instead of waiting until a limit-cycling condition develops that forces a maintenance shut-down at an inconvenient time.

**Supplemental Cooling**

Some reactors have two sources of cooling, at different costs. For example, cooling water can be used up to the point where its valve is fully open, and then a supplemental medium such as chilled water may be used for additional cooling. If the two media can be mixed, then accommodating the additional source is as simple as sequencing the two valves. For example, the cooling-water valve could open from 50 to 25% of controller output, and the chilled-water valve from 25 to 0.

However, the media are likely to be separated from each other to avoid cross-contamination, with auxiliary cooling by chilled water passing through an internal tube bundle, and cooling water circulated through the jacket. This complicates...
a control system that features cascade control of jacket outlet temperature. The cascade system should be retained for its effectiveness, and the supplemental cooling manipulated to keep the jacket temperature operating in its control range.

This is done by the use of a valve-position controller (VPC) connected to the secondary output, as was shown in Figure 8.9o in the previous section. Using integral-only control, it manipulates the chilled-water flow to keep the cold-water valve about 90% open, which corresponds to a controller-output signal of 5% (its range being 50–0%).

As long as the heat load stays in the range of the cold-water valve, the chilled-water valve would remain closed. But when the VPC set point is passed, the chilled-water valve will be opened as necessary to match the load. This loop is not fast, but it need not be any faster than the expected load changes, because the jacket-temperature loop is always in control.

Whether the additional cost of the chilled water can be justified depends on the demand for product. In most cases where supplemental cooling is used, it is only needed during peak load, which only represents part of a typical batch operation.

References
4. Ibid., pp. 324–325.

Bibliography