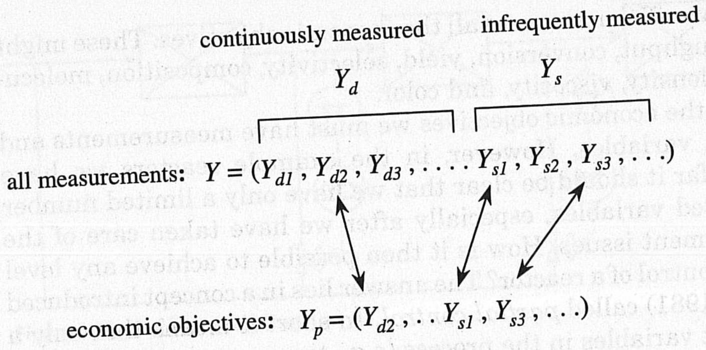

Figure 4.30 Classification of measured variables.

ously or with a sample time that is small compared to the process time constant. Examples are temperature, pressure, level, density, and many on-line analyzer measurements. The rest of the measured variables are denoted Y_s (s for slow, sampled, or steady-state), such that $Y_s + Y_d = Y$. Examples of members belonging to Y_s are infrequent laboratory measurements and yield and conversion calculations based on mass balances. The list of economic variables or specifications is given the symbol Y_p (p for product or property). These variables form another subset of Y where we borrow some variables from Y_d and some variables from Y_s. Figure 4.30 summarizes the classification of measured variables.

We can make a similar classification around U and W. For instance, control valves belong to the set U_d, whereas the regeneration of a packed-bed catalyst would be classified as U_s. Similarly, measurements of the reactor feed flow and temperature belong to W_d, while a once-per-shift analysis of the reactor feed composition belongs to W_s.

4.6.3 Partial control

Control engineers know that it takes one manipulated variable for each measured variable we wish to control to setpoint. When the number of controlled variables equals the number of manipulated variables we pair up the different variables and use PI controllers for regulation. Sometimes we are fortunate to have more manipulated variables than control specifications. We can then optimize the use of the manipulators while controlling to setpoint (e.g., valve position control). Sometimes, however, the number of control objectives exceeds the number of available manipulators and we cannot control all variables to setpoint. This is when the concept of partial control is useful.

There are two premises behind partial control. The first is that many of the economic objectives are correlated. This means that by controlling some of the measured variables we can bring the rest into an acceptable range of compliance. For example, in a reaction $A \rightarrow B \rightarrow C$ we can usually improve the yield of B by limiting the conversion of A. Since yield and conversion are economic objectives we can satisfy both within a range by controlling only one variable. The reason this principle works, we believe, is that the state variables in process systems (especially reactors) are intimately linked through stoichiometry, kinetics, thermodynamics, and mixing.

The second premise behind partial control is the concept of dominance. We introduced this concept earlier when we discussed reaction rate expressions. There we mentioned that temperature often plays a dominant role for the rate of reaction especially when the activation energy is high. We also mentioned that a key component in the rate expressions can dominate the rate particularly when the component has a low concentration (e.g., limiting reactant or the catalyst).

If we accept these two premises, the implementation of partial control involves two conceptually simple steps:

1. Control all dominant variables to setpoint with feedback controllers using manipulators with a rapid response. This ensures *unit control*.
2. Adjust the setpoints of the controlled variables such that all economic objectives are brought within acceptable ranges. This is partial control. 2

In symbols we can express partial control as follows:

$$Y_{p,\min} < Y_p < Y_{p,\max} \tag{4.28}$$

$$Y_p = M^s(U_s,\ Y_{cd}^{\text{set}},\ W) \tag{4.29}$$

where $M^s(\cdot)$ stands for a steady-state, correlation model.

The economic objectives Y_p can be positioned in the desired range when there is a strong relationship between the economic objectives and the measured inputs W, the steady-state manipulators U_s, and the setpoints of the controlled, dynamic variables Y_{cd}^{set}.

A few comments about the method are warranted. The controlled (dominant) variables, Y_{cd}, should be measured such that they belong to the set Y_d for rapid control. Similarly, the manipulators in the feedback control loops should belong to the set, U_d. The feedback controllers should have integral action (PI controllers). These can be tuned with minimal information (e.g., ultimate gain and frequency from a relay test). The model M^s is usually quite simple and can be developed from operating data using statistical regressions. This works because the model includes all the dominant variables of the system, Y_{cd}, as independent variables by way of their setpoints, Y_{cd}^{set}. The definition of dominance is that the whole state vector is strongly correlated to these few variables.

On the surface it might appear that partial control does not require a first-principles model for its implementation. After all, M^s is a regression model and controller tuning is based on relay-feedback information. For simple systems this may be correct. However, for most industrially relevant systems it is not intuitively obvious what constitutes the dominant variables in the system and how to identify appropriate manipulators to control the dominant variables. This requires nonlinear, first-principles models. The models are run off-line and need only contain enough information to predict the correct trends and relations in the system. The purpose is not to predict outputs from inputs precisely and accurately, but to identify dominant variables and their relations to possible manipulators.

Let's look at some examples. First consider the vinyl acetate reactor discussed in Chap. 11. It is a plug-flow system with external cooling. To satisfy the heat balance we have already proposed to close one loop around the reactor, namely between the reactor exit temperature and the coolant temperature (steam pressure). This provides us with one setpoint, Y_{cd}^{set}, that we can use to meet economic objectives, Y_p, provided exit temperature is a dominant variable.

Before we investigate the dominance aspects of the vinyl acetate reactor we ask "What are the economic objectives?" As a minimum we would like to control the production rate of vinyl acetate, T/P, and the selectivity SEL to vinyl acetate. Therefore, any dominant variable should have a significant impact on these economic objectives. Figure 4.31 shows how the objectives vary with reactor exit temperature. It is clear that we have identified a dominant variable and that it is possible to set the reactor exit temperature such that both the production rate and the selectivity fall within certain ranges for given values of the feed conditions, W, and a given level of catalyst activity, U_s. This is the meaning of partial control.

To complete the picture we should investigate if there are more dominant variables in the system. We have already touched on this issue in the section on reaction rates. There we noted that the acetic acid concentration to the reactor is not dominant. We can also argue that the ethylene partial pressure is not likely to be a dominant variable since ethylene enters the reactor in large excess. However, oxygen is the limiting component and it plays a role in the main reaction as well as in the side reaction. Oxygen therefore affects the economic objectives and is considered dominant. Feedback control of the oxygen concentration to the reactor is necessary if we want complete control of the unit.

The next example is the HDA reactor presented in Chap. 10. It is an unpacked gas flow reactor operated adiabatically so the reactor does not have any heat management control loops associated with it. First,

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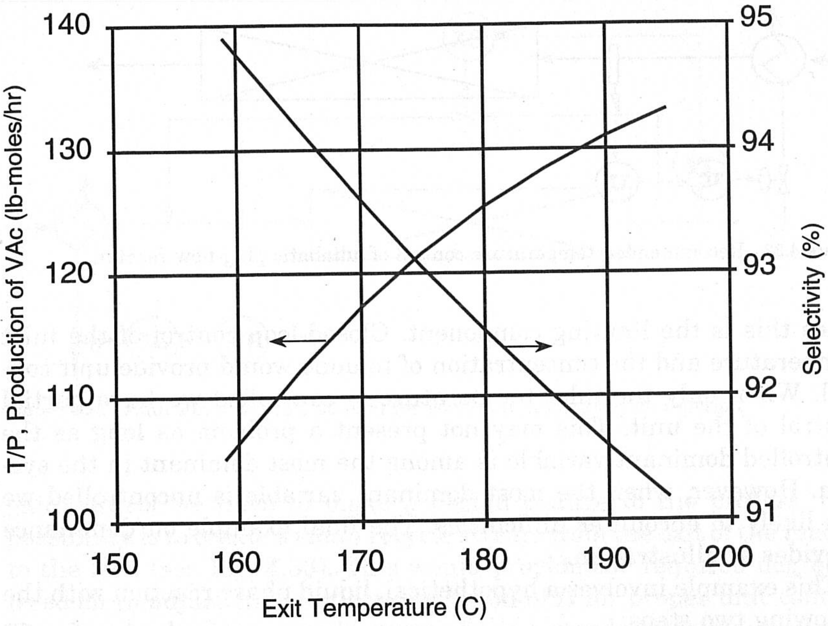

Figure 4.31 Production rate and selectivity as functions of vinyl acetate reactor temperature.

we examine the economic objectives. We would like to set the production rate. We are also interested in the yield of benzene from toluene. We use yield instead of selectivity since it is the product, benzene, that forms the by-product, diphenyl.

It is easy to imagine that inlet temperature might be a dominant variable for exothermic, adiabatic plug-flow reactors when the reactions have reasonably high activation energies. First, these systems require a minimum inlet temperature to get the reactions going at all. Second, the exit temperature depends directly upon the inlet temperature through the adiabatic temperature rise. Last, the response to inlet temperature should be unique since there are no issues of multiplicity or parametric sensitivity for the reactor in isolation. Therefore, to close a loop around $Y_{cd} = T_0$ we need only identify the appropriate manipulated variable. This variable should be able to alter the heat content of the feed stream as shown in Fig. 4.32. Since the HDA reactor requires a furnace for its operation, the choice is not difficult; we use the heat input to the furnace to control the reactor inlet temperature. The only complications we might experience is when the furnace is made small due to a very high level of heat integration in the plant. Inlet temperature control may suffer under those circumstances. We shall have more to say about this in Chap. 5.

The HDA reaction is also dominated by the partial pressure of toluene

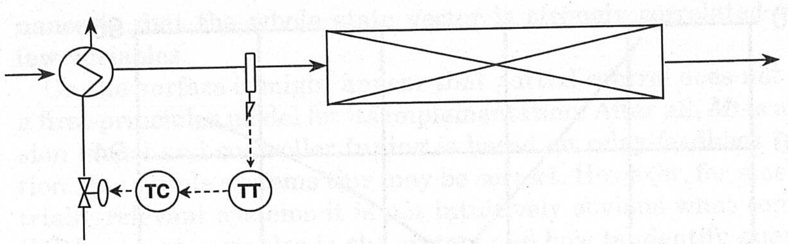

Figure 4.32 Recommended temperature control of adiabatic plug-flow reactor.

since this is the limiting component. Closed-loop control of the inlet temperature and the concentration of toluene would provide unit control. When only the inlet temperature is controlled we have partial control of the unit. This may not present a problem as long as the controlled dominant variable is among the most dominant in the system. However, when the most dominant variable is uncontrolled we are likely to encounter difficulties. The final example on dominance provides an illustration.

This example involves a hypothetical, liquid phase reaction with the following two steps:

$$A + 2B \rightarrow 3B + C \qquad r_1 = k_1 C_B^2 C_A$$

$$B \rightarrow D \qquad r_2 = k_2 C_B$$

Note that the first reaction is autocatalytic in component B. Reactant A is the limiting component. Component B is the desired product while C and D are by-products. Both reactions have moderate heats of reaction and relatively low activation energies. To maximize the yield of B, a plug-flow reactor was selected. The economic objectives are throughput and yield. What is the appropriate partial control scheme for this reactor?

Following the arguments around the HDA reactor, we conclude that inlet temperature should be a dominant variable. However, in this case it is not strongly dominant due to the low activation energies. In other words, k_1 and k_2 do not vary much with temperature. Instead, the most dominant variable is C_B, the concentration of product along the reactor. The component B enters the reactor at a low concentration and dominates the rate of both reactions at least until most of the reactant A is consumed. Furthermore, the main reaction is autocatalytic in B such that the rate of formation of B depends upon it own concentration. Unit control therefore requires that we find a manipulated variable that allows us to vary the inlet concentration of B to the reactor. Without such a loop the output from the reactor would depend entirely on minute variations in the feed concentration, which would be unpredictable. To

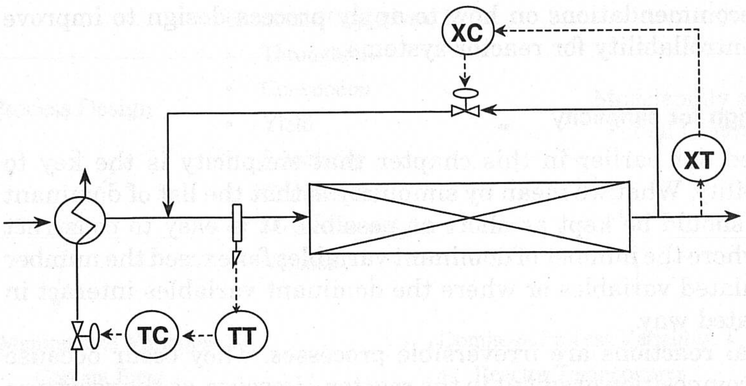

Figure 4.33 Addition of recycle stream for control of autocatalytic reaction.

gain control we have to make a design change to the process. One possibility is to create a small recycle stream from the exit of the reactor to the feed (see Fig. 4.33). This would provide the required degree of freedom to adjust the inlet concentration of B for proper unit control. The drawback of the recycle stream from a steady-state standpoint is that we give the recycled product B a chance to convert into undesirable by-product D. The steady-state yield will decline but the reactor is under unit control. This is another example of the trade-off between steady-state economics and controllability that we frequently encounter.

4.7 Design and Control

4.7.1 Process design versus controller design

As we explained in Chap. 1, process and control engineers have traditionally had distinct and different roles in designing a plant. Process engineers are present from project start and are responsible for flowsheet development and equipment design, whereas control engineers enter later and work with the designed process to specify sensors, valves, and the control system. We believe that process engineers impact controllability far more than control engineers can do through controller design. In other words, a small change to the process (such as providing 20 percent more surface area for cooling or providing a small recycle stream for unit control) can make the difference between an unstable reactor and a well-behaved one. Similarly, no amount of Kalman filtering, model predictive control, or nonlinear control theory can make up for a missing control degree of freedom. We now give some specific recommendations on how to apply process design to improve process controllability for reactor systems.

4.7.2 Design for simplicity

We pointed out earlier in this chapter that simplicity is the key to controllability. What we mean by simplicity is that the list of dominant variables should be kept as short as possible. It is easy to construct reactors where the number of dominant variables far exceed the number of manipulated variables or where the dominant variables interact in a complicated way.

Chemical reactions are irreversible processes. They occur because there is a composition gradient in the reactor. However, as the reactions proceed they can create other gradients such as pressure profiles, mixing gradients, and temperature profiles. The thermodynamic variables affected by the various gradients also influence the chemical kinetics so that the whole system can be coupled in a complex way. This coupling, or feedback, promotes the chances for multiplicity and open-loop instability. The more dominant variables that are affected and the more of those that interact, the less are our chances of controlling and modeling the system. This is particularly true when the stoichiometry and kinetics are complex as well. In fact, we would like to offer the following recommendation based on our own experiences but nicely formulated by Shinnar (1997): *Simple reactions can be carried out in complex reactors, but complex reactions need simple reactors.*

So, what kind of complications should be avoided? The most prominent ones are uncertain hydrodynamics, mixing, and mass transfer. These phenomena are difficult to predict by themselves and when they interact and affect the rate of reaction we may have an uncontrollable reactor. Fogler (1992) gives an example of how the dominant variables can change according to the rate controlling step in a slurry reactor. For example, when the gas-liquid mass transport controls the rate, the dominant variables are stirring rate and the partial pressure of reactant in the gas phase. On the other hand, when the chemical reaction governs the rate, the dominant variables are temperature, amount of catalyst, and liquid phase reactant concentration. We can only begin to imagine how well such a reactor would meet stated economic objectives if it operated in the gas mass transfer regime with a control system designed for kinetic control.

4.7.3 Design for partial control

Once the most appropriate reactor system has been chosen, the next important design issue to consider is how to provide enough manipulated variables to ensure adequate partial control. The first step in this ess design to improve

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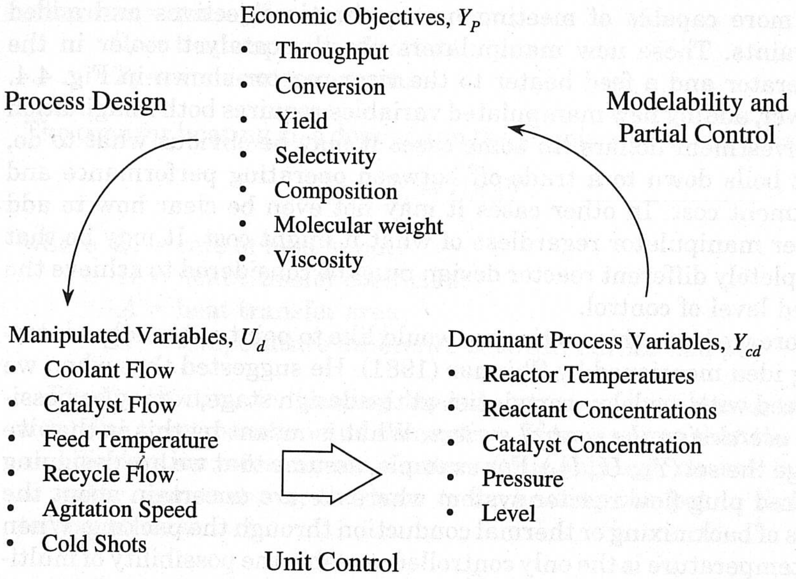

Figure 4.34 Relationship among economic objectives, dominant variables, and manipulated variables.

procedure is to identify the dominant variables, since they are the ones that should be part of the primary control structure. It may not be necessary to control all dominant variables to stabilize the unit. For example, with sufficient hydrogen recycle, the HDA reactor can be operated by using only the inlet temperature for unit control. On the other hand, the autocatalytic plug-flow reactor described above requires more than inlet temperature control to hold the unit in a defined state. Once the minimum number of dominant variables is identified for stable unit control, we must check if this set is sufficient for partial control of the economic objectives. If not, we provide additional measured and manipulated variables to improve the performance. Figure 4.34 illustrates the relationship between economic objectives, dominant variables, and manipulated variables.

Arbel et al. (1997) give a detailed account of this procedure applied to a fluidized catalytic cracker (FCC). They show that unit control is possible when only one of the four dominant variables is under feedback control. The effectiveness of the partial control scheme is limited in satisfying the economic objectives when only one dominant variable is in closed-loop control. Superior reactor performance is achieved when all four dominant variables in the reactor are used. However, this requires manipulated variables that were not part of older FCC designs. The new manipulators have been added on modern units to make them more capable of meeting new economic objectives and added constraints. These new manipulators are the catalyst cooler in the regenerator and a feed heater to the riser reactor shown in Fig. 4.4. However, adding new manipulated variables requires both imagination and investment dollars. In some cases it may be obvious what to do, and it boils down to a trade-off between operating performance and investment cost. In other cases it may not even be clear how to add another manipulator regardless of what it might cost. It may be that a completely different reactor design must be considered to achieve the desired level of control.

Before we leave this section we would like to point out another interesting idea mentioned by Shinnar (1981). He suggested that when we are faced with model uncertainties at the design stage, it may be possible to *overdesign the control system*. What is meant by this is that we enlarge the set (Y_{cd}, U_s, U_d). For example, assume that we are designing a packed plug-flow reactor system where we are uncertain about the effects of backmixing or thermal conduction through the packing. When inlet temperature is the only controlled variable the possibility of multiple steady states and open-loop instability becomes a reality. To guard against these uncertainties we could consider alterations to the basic design that would allow us to control more dominant variables, in this case temperatures and compositions along the length of the reactor. We could use intermediate coolers or cold shots as the new manipulated variables required for control of the additional control points.

Similarly, the uncertainties around the rate controlling step for the slurry reactor may also be dealt with through overdesign of the control system. In that case it may be prudent to provide a couple of control loops that could control the addition of reactant gas through some high-pressure jet spargers or provide a variable speed agitator.

4.7.4 Design for responsiveness

When the unit control structure has been established, we would like to design the process such that the control loops are as responsive as possible. Interestingly enough, we can get clues on how to do this from the area of irreversible thermodynamics. The details are spelled out in Appendix A but let us give a brief introduction here, based on a very simple analog.

Assume we want to heat a pot of water on the stove from room temperature to a particular temperature below the boiling point. The time it takes to heat the water depends, in part, on how much heat Q_s is contained (stored) in the water when we reach the final temperature T_1:

$$Q_s = mC_P(T_1 - T_0) \tag{4.30}$$

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where m = mass of water in pot
C_P = heat capacity of water
T_0 = ambient temperature

The time for heating also depends on the supply of heat from the burner

$$\dot{Q}_s = UA\Delta T \tag{4.31}$$

where $\dot{Q}_s$ = rate of heat supply
U = heat transfer coefficient
A = heat transfer area
ΔT = temperature difference between burner and pot

Finally, the time for heating depends on rate of heat loss $\dot{Q}_d$ (dissipation) due to evaporation and convection. If we assume that the supply and dissipation rates remain constant (true only over narrow intervals of water temperature), the time t_h for heating the pot to the target temperature is

$$t_h = \frac{Q_s}{\dot{Q}_s - \dot{Q}_d} \tag{4.32}$$

As we all know, the heating time is reduced when there is little water in the pot, when the target temperature is low, when the burner is hot, and when there is a lid on the pot. Assume now that we took all those measures and managed to overshoot the target temperature. What do we do then? We turn off the burner, remove the lid, and probably stir to improve the rate of heat dissipation. The time it takes for the water to settle to the correct temperature is

$$t_c = \frac{Q_s^E}{\dot{Q}_d} \tag{4.33}$$

where t_c = cooling time and Q_s^E = excess heat stored in water. Once we arrived at the correct water temperature, we can hold it there by matching the supply to the dissipation rate, $\dot{Q}_s = \dot{Q}_d$.

It is intuitively clear in this example [and also seen in Eqs. (4.32) and (4.33)] that the response time is a direct function of the storage of heat and inversely proportional to the rate of heat removal or supply. From a control standpoint we can shorten the response time by affecting the supply and dissipation rates.

It turns out that the water pot example is a nice analog for a general process system such as a reactor. In the process system we characterize the energy storage with the thermodynamic state function *exergy B*, instead of heat Q_s. Heat is of course not a general thermodynamic state function but it plays the role of one in the water pot example. In the general process we replace the heat dissipation rate $\dot{Q}_d$, by the *exergy destruction rate* $T_0\dot{\sigma}$. The rate of exergy destruction is directly related to the rate of entropy production $\dot{\sigma}$ in the universe as a result of performing our process. We can show that the response rate of a process control loop is inversely proportional to the rate of entropy production caused by the manipulated variable. In other words, if we can find manipulated variables that strongly affect the rate of entropy production we can achieve responsive control.

We show in Appendix A that the rate of entropy production depends upon the product of fluxes and gradients. Fluxes and gradients are connected in the sense that a gradient is capable of generating a flux. For example, heat flows across temperature gradients and material flows across composition gradients. By manipulation of the fluxes or the gradients we can affect the rate of entropy production.

Temperature control of exothermic reactors involves manipulating the temperature gradient between the process and the coolant. Whenever we can affect the gradient significantly we are likely to have a responsive control loop. When the jacket temperature is affected by coolant flow, inlet temperature, or boiling point, it is easy to see that the flux can be changed more in designs with larger heat transfer areas. This follows directly from the heat transfer equation [e.g., Eq. (4.31)]. A small change in the coolant temperature will amount to a large relative change in ΔT and cause a major change in the heat flux. The product of heat flow and temperature gradient affects the entropy production rate and hence the time response for control.

Luyben and Luyben (1997) give several reactor examples where a large heat transfer area is beneficial for temperature control. The classic example is the scale-up of a jacketed CSTR. A small pilot plant reactor has a large heat transfer area compared to the reactor volume and temperature control is excellent. When the reactor is scaled to commercial size, the surface-to-volume ratio becomes unfavorable for control. The large heat release coupled with a relatively small UA forces the coolant rate to be high and the gradient ΔT to be large. Changes in the coolant rate now cause only minor relative changes to the gradient and the heat flux. The change in entropy production per change in cooling rate flow is small and control suffers.

Another example cited in Luyben and Luyben (1997) is when a large jacketed CSTR is replaced by several smaller CSTRs in series. For most reactions, a series of CSTRs has a lower total volume than a single CSTR for the same production rate and operating temperature. This smaller total reactor volume produces a smaller surface area and a larger ΔT, resulting in poor temperature control, particularly in the first reactor.

We have also seen the importance of a large heat transfer area in

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other examples given in this chapter. For example, we showed that the stability conditions for a cooled CSTR are

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

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

When we insert the proper terms from the Jacobian matrix we find the following set of inequalities must be satisfied for open-loop stability.

$$(V\rho C_P + M_w C_w) \cdot \frac{1 + \bar{k}\tau}{\tau} + F\rho C_P + UA >$$

$$\bar{k}\bar{C}_A V(-\Delta H)E_a/R\bar{T}^2 >$$

$$\frac{1 + \bar{k}\tau}{\bar{k}\tau} \cdot (-F\rho C_P - UA + \bar{k}\bar{C}_A V(-\Delta H)E_a/R\bar{T}^2)$$

We see by inspection that stability can always be ensured by making *UA* sufficiently large.

The principle of designing for small gradients is not limited to heat transfer examples. It applies to other thermodynamic gradients as well. For example, sparged reactors with fast reactions benefit from small gas bubbles with a large surface area to promote mass transfer. Under those circumstances minor variations in the partial pressure of reactants give a rapid response in overall reaction rates.

Chemical reactions are also influenced by gradients in the chemical potentials of the reactants and products. The chemical reaction gradient is called the *affinity*, A_j. The affinity for reaction j containing n components is

$$A_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i$$

where ν_{ij} = stoichiometric coefficient for component i in reaction j and μ_i = chemical potential of component i. The flux belonging to A_j is the rate of reaction, r_j.

Consider, for example, a simple reaction $A \rightarrow B$ with a rate expression $r_1 = kC_A$. The affinity for this reaction is

$$A_1 = -(-1 \cdot \mu_A + 1 \cdot \mu_B) = \mu_A^0 - \mu_B^0 + RT \ln \frac{C_A}{C_B}$$

A small affinity implies a low concentration of component A and a large concentration of component B, in other words, a high degree of conversion. If we consider controlling the reactor by adjusting the concentration of reactant we would get the fastest response in designs using large, backmixed reactors with nearly complete conversion of reactant. The worst response is obtained in small plug-flow systems with low per-pass conversion of reactant. A large one-pass reactor is easier to control than a smaller reactor in a recycle loop. We demonstrated this in Chap. 2. There we also showed that a reactor followed by a stripping column with recycle is cheaper than one large reactor. Again, this is an important example of the trade-off between steady-state investment cost and controllability.

4.8 Plantwide Control

So far we have dealt with control of reactors as isolated units. We now examine how reactors are controlled when they are part of an integrated plant. In principle, nothing new is introduced beyond the useful concepts involved in partial control. We can delineate among three cases:

1. All dominant variables are controlled at the unit level with manipulated variables local to the reactor.
2. Some dominant variables are controlled at the unit level.
3. The reactor is not controlled at the unit level.

Case 1 is desirable from the standpoint that it eliminates interactions from the rest of the plant. In other words, it is transparent to the reactor whether it is an isolated unit or part of a process with recycles. The economic objectives of the process are satisfied through partial control by adjusting the setpoints of the feedback loops. We can argue that the vinyl acetate reactor discussed in Chap. 11 falls in this category. The dominant variables are reactor exit temperature and oxygen inlet concentration. Both of these variables are controlled at the unit, making the reactor resilient against disturbances from the separation system.

Case 2 includes many of the example systems studied in this book. For example, reactors with temperature as the only controlled variable fall into this category. Also, the isothermal ternary scheme CS4 shown in Fig. 2.13*a* has a local composition controller on one of the dominant variables, the composition of component *A*. However, Case 2 is characterized by the fact that other dominant variables are not controlled at the reactor. Instead, the plantwide control structure plays a significant role in its ability to influence these uncontrolled variables. When the uncontrolled compositions become disturbances and the controlled dominant variables are too weak, we have difficulties. On the other hand, the plantwide control structure can be arranged to provide indirect control of the dominant composition variables, thereby augmenting the unit control loops. The HDA process provides a good illustration. The dominant variables are reactor inlet temperature and toluene composition. Only inlet temperature is controlled locally by the heat added to the furnace. If we let the toluene composition be a disturbance to the reactor we may have serious control difficulties especially with a small furnace. However, when we arrange the plantwide control loops for indirect control of the toluene feed concentration, we enlarge our opportunities for partial control. It is now possible to use a combination of setpoints for the inlet temperature and the toluene recycle to impact the economic objectives of throughput, yield, quality, etc.

Case 3, finally, provides the ultimate challenge for the plantwide control structure. Here, all the dominant variables in the reactor are influenced by the actions of controllers elsewhere in the plant. Now it becomes imperative that the plantwide controllers provide indirect control over all or most of the dominant variables. Several examples in Chap. 2 demonstrated this. As we showed in Chap. 2, it is very easy to configure schemes that turn the dominant variables into reactor disturbances. These schemes don't work at all. Consequently, we do not recommend building plants without local unit operation control for the reactor.

4.9 Polymerization Reactors

4.9.1 Basics

Polymers are long-chain molecules composed of repeated smaller units called *monomers*. The term *polymer* spans an enormous spectrum of substances that find widespread use in virtually all aspects of modern society. Polymers range from high-volume commodity types (polyethylene, polystyrene, etc.), to synthetic fibers (polyesters, polyamides, etc.), to engineering resins (polycarbonates, polyacetals, etc.), and beyond.

Polymerization reactors are generally one part of a large process involving monomer production and purification; polymer production; polymer recovery, isolation, and finishing; and monomer recovery and recycle. The general principles of plantwide control fit into continuous polymer processes because of this integration. Many of the concepts presented in this chapter directly apply to polymer reactors. As noted earlier, entropy decreases in polymerization reactions, which means that they are typically highly exothermic to satisfy Eq. (4.2). Reactor design for agitation and heat removal are crucial, particularly when the polymeric materials become highly viscous. In some cases the reactions are reversible at the normal operating temperatures, so the system ends up at equilibrium.

The basic concepts of modeling, open-loop behavior, reactor control, and plantwide control apply to polymer processes. It would be folly to attempt a comprehensive treatment of the subject in this text. We refer

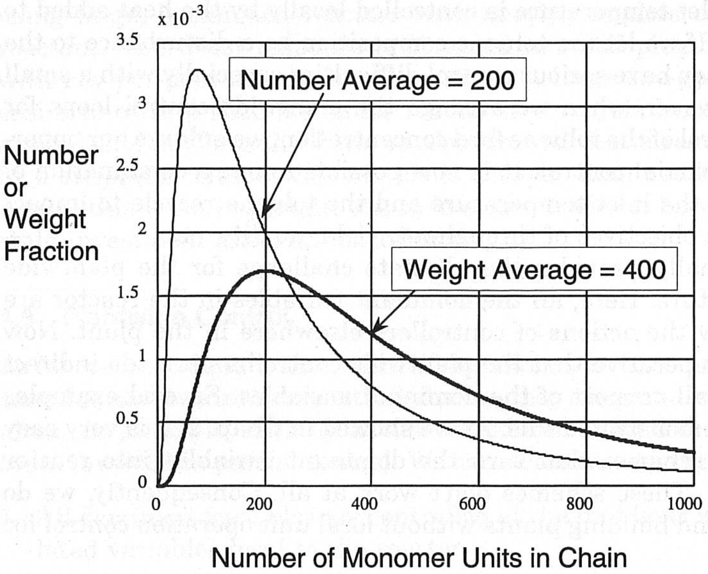

Figure 4.35 Number and weight distributions for polymer.

the interested reader to Grulke (1994) and other excellent books on polymer science and engineering. However, we want to highlight in this section a key feature about polymerization reactors that is unique from other kinds of reactors.

The key feature of any polymer is that all chains are *not* of the same length. This gives rise to a *distribution* of various chain lengths (or molecular weights). This distribution can be characterized on the basis of number or weight fraction (Fig. 4.35). The number average (M_n) and weight average (M_w) molecular weights (or chain lengths) are the values where the areas under the distribution curves are equal to the left and right.

Certain important properties of polymers are directly related to the average chain length and the distribution. One of particular importance is the viscosity. This affects the flowability of the polymer and the kinds of applications where it can be used (injection molding, blow molding, fiber spinning, sheet formation, coating, etc.).

We are therefore concerned in polymer reactors to produce the desired average number of monomer units per chain and also the distribution (i.e., low and high molecular weight tails). The *polydispersity* PD is the measurement of the distribution and is the ratio of the weight average to number average molecular weights.

$$\mathrm{PD} = \frac{M_w}{M_n} \tag{4.34}$$

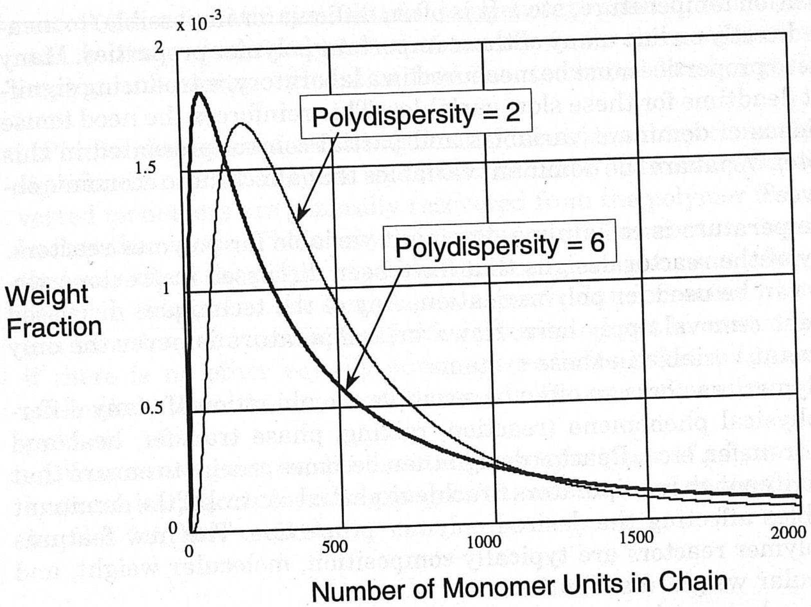

Figure 4.36 Spread of molecular weights.

A polymer may not have many high-molecular-weight molecules. They have little effect on the number average but contribute significantly to the weight average. As illustrated in Fig. 4.36, two polymers with the same weight average molecular weight can have completely different properties because of the difference in the distribution. The polymer with the lower number average molecular weight has a larger spread in the distribution, a longer high molecular weight tail, and a larger value of polydispersity. The *Flory distribution* is called the most probable and has a polydispersity equal to 2.

Other polymer properties also are important in addition to molecular weight and viscosity. If the polymer comes out of solution in the reactor as solid particles, then we would like to have the desired particle size distribution. Polymers composed of several different monomers, or *copolymers*, must have the appropriate compositions and segments along the polymer chain. The color of the polymer is important in some applications, as is the temperature of phase transitions, among other properties.

4.9.2 Dominant variables

Hence the key economic control objectives for polymer reactors are typically average molecular weight, polydispersity, viscosity, composition, partical size distribution, and production rate (plus color, phase transition temperature, etc.). It is often difficult (or impossible) to measure directly on line many of these important polymer properties. Many of these properties must be measured in a laboratory, introducing significant deadtime for these slow variables. This reinforces the need to use the ideas of dominant variables and partial control presented in this chapter. What are the dominant variables that affect these economic objectives?

Temperature is certainly a dominant variable for polymer reactors. Many of the reactor designs that have been discussed in previous sections can be used for polymerization. Any of the techniques discussed for heat removal apply here. However, temperature is never the only dominant variable in these systems.

Polymer reactors can often be a complex combination of many different physical phenomena (reaction, mixing, phase transfer, heat and mass transfer, etc.). Reactor design then becomes crucial to ensure that we have enough manipulators to achieve partial control of the dominant variables affecting the desired polymer properties. The new features for polymer reactors are typically composition, molecular weight, and molecular weight distribution.

For polymers that come out with the Flory distribution, we don't have a handle to control polydispersity. However, we almost always have a way to control conversion by using temperature, initiator or catalyst, or chain transfer agents. One equation that helps in looking at partial control is the relation between the degree of polymerization (DP) and conditions within the reactor:

$$\mathrm{DP} = \frac{\text{rate of propagation}}{\text{rate of chain transfer} + \text{rate of termination}} \tag{4.35}$$

DP is the average number of monomer (or repeat) units per polymer chain and so is directly related to molecular weight (or viscosity). This relationship shows that we must have control over variables that have a significant effect on propagation, chain transfer, and termination to achieve the desired polymer properties. What are these variables? They are the same as those we have discussed throughout this chapter: temperature, reactant monomer concentrations, concentrations of chain transfer agents or other impurities that affect polymerization, initiator or catalyst concentration, residence time, etc.

Polymer reactor control then boils down to controlling all dominant variables to setpoint using manipulators with a fast response and then adjusting the setpoints of the controlled variables to achieve the desired economic objectives. The trick is to determine the dominant variables and manipulators in addition to their relationships. Some key manipulators are heat removal (for externally cooled systems) or conversion control (for adiabatic systems) for temperature control; monomer, solvent, initiator, and catalyst feed stream flows (or compositions) to the reactor; and reactor effluent or feed flow to control level or residence time.

Plantwide issues of recycle and component inventory control play a significant role for polymer reactors. Because of their value, unconverted monomers are generally recovered from the polymer for recycle back to the reactor. These recycle streams most often contain impurities that can affect the polymerization (molecular weight, conversion, composition, color, etc.). In some cases a particular component impurity can be a dominant variable. If this impurity cannot be controlled and if there is no other equally dominant variable present that can be controlled, then the result will usually be an undesirable polymer product.

We are now going to discuss the two major types of polymerization systems, step growth and chain growth, and show what the difference implies for their control.

4.9.3 Step growth

Stepwise polymerization occurs from the intermolecular reaction of two different reactive end groups and the production of a low-molecular-weight “leaving group.” Nylon 6,6 is an example of a step-growth polymer. The polyamide is made from the reaction of adipic acid and hexamethylene diamine, both of which have two reactive end groups. Water is the leaving group in this system.

$$\begin{aligned}&\mathrm{HOOC-(CH_2)_4-COOH+H_2N-(CH_2)_4-NH_2}\\&\qquad\rightleftharpoons\mathrm{HOOC-(CH_2)_4-CONH-(CH_2)_4-NH_2+H_2O}\end{aligned}$$

This is an equilibrium reaction at typical operating conditions, which has several consequences for reactor design and control. Temperature control is of course important for its effect on the equilibrium conditions. In step-growth polymerization, several stages are often used to eliminate the volatile leaving group and allow the reaction to proceed to high conversion and molecular weight. For these systems material recycle is not typically a major factor.

For the liquid-phase reactor shown in Fig. 4.37, monomer feed is introduced and the effluent stream controls the level (residence time). Heat is removed via cooling water. We want to remove the water to push the equilibrium to the right and increase conversion. Due to its volatility, it would be natural to remove the water vapor from the reactor to control pressure.

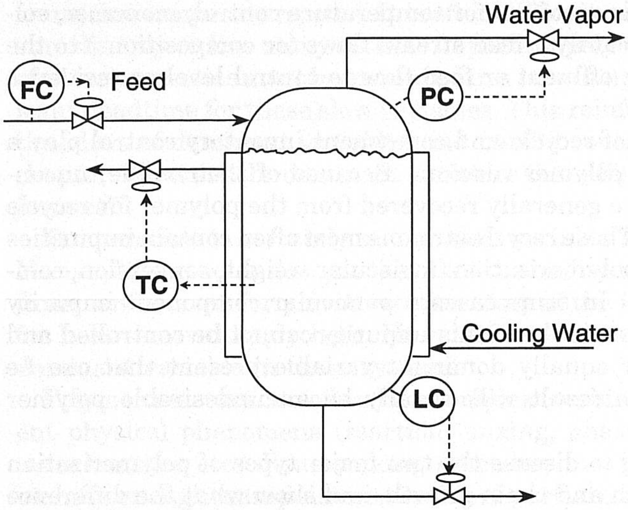

Figure 4.37 Control of step-growth polymerization reactor.

4.9.4 Chain growth

Chain-growth polymerization does not produce a leaving group. Rather, it results from the coupling of reactive centers (often free radicals or ions) adding monomer units. Polyethylene is an example of a chain-growth polymer, where the propagation step is

$$\mathrm{R - CH_2 - CH_2\bullet + CH_2 = CH_2 \rightarrow R - CH_2 - CH_2 - CH_2 - CH_2\bullet}$$

In this system conversion affects polymer properties. We typically cannot go to high conversion because of molecular weight or heat removal constraints (if adiabatic). There may also be a large increase in viscosity that affects the heat removal, agitation, and processability of the polymer solution. Here conditions dictate the kind of molecular weight distribution. The polymer is often affected by impurities and chain transfer agents that determine the amount of branching and termination.

For an adiabatic reactor, we may be able to control temperature and conversion using the initiator feed flow (Fig. 4.38). Incomplete conversion introduces recycle streams for the monomer. Because of the effect of chain transfer agents, we often must be able to measure the feed compositions to the reactor. Further, we must know what the chain transfer agents do if they are dominant variables to have any chance of controlling the molecular weight. So our control will only be as good as our correlations or models. Hence in polymer reactors we often have to use what is basically “steady-state” control on the setpoints of the dominant variables to achieve many of the control objectives that de-

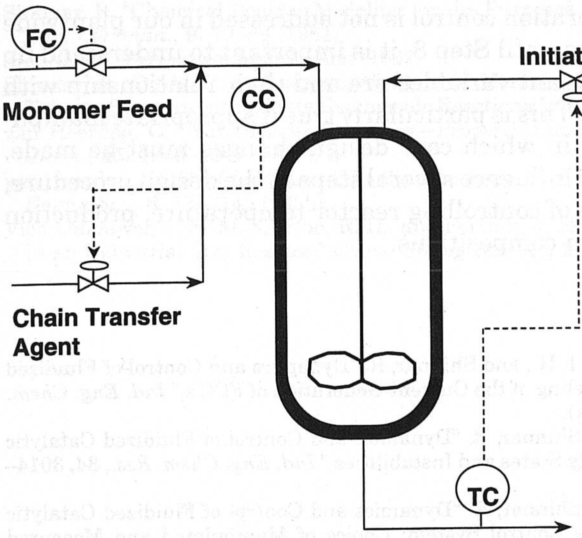

Figure 4.38 Control of adiabatic chain-growth polymerization reactor.

pend upon infrequent laboratory measurements (the notion of modelability in Fig. 4.34).

4.10 Conclusion

Here we have dealt with the control of chemical reactors. We covered some of the fundamentals about kinetics, reactor types, reactor models, and open-loop behavior. In particular we have shown that reactors with recycle or backmixing can exhibit multiple steady states, some of which are unstable. Nonlinearities in reactor systems also frequently give rise to open-loop parametric sensitivity.

Most importantly, we introduced the ideas of dominance, effective degrees of freedom, and partial control for chemical reactors. In essence, dominant variables are controlled by manipulators with a fast response and the setpoints are adjusted to achieve the economic objectives. These notions are useful in this context, but they can be utilized more widely for other unit operations.

Temperature is commonly the most dominant variable in reactor systems. Since many chemical reactors are exothermic, controlling the dominant variable in these systems amounts to removing the exothermic reaction heat through temperature control. We gave many examples of how that is done. In cases where temperature is not the most dominant variable, compositions typically dominate. In this case unit control is not localized to the reactor since composition control is affected by other parts of the plant.

Even though unit operation control is not addressed in our plantwide control design procedure until Step 8, it is important to understand up front what all the dominant variables are and their relationship with potential manipulators. This is particularly true if appropriate manipulators are unavailable, in which case design changes must be made. The dominant variables influence several steps in the design procedure, in particular our choice of controlling reactor temperature, production rate, and recycle stream compositions.

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