Process Design with Complex Nonlinearities[*]

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Abstract

As process designs move into or closer to regimes of complex nonlinearity, they become more sensitive to model uncertainties and disturbances. This paper examines process designs that operate closer to or within these regimes often to achieve greater profitability and improved performance. Emphasis is placed on developments over the past decade. Considerations for process controllers in the operation of such processes are elucidated.

1   Introduction

Nearly a decade ago, Seider and coworkers (1990) examined incidences of overdesign that arise when protecting against regimes of complex nonlinear operation that can occur in exothermic and isothermal reactors, thermally coupled and azeotropic distillation towers, supercritical extractors, and other processes. They provided examples in which key parameters were constrained and the degree of back-mixing reduced to avoid operation near or within regimes having multiple steady states and periodic or chaotic behavior. They pointed out that in designing these processes, it is important to locate the range of the design parameters over which complex operating regimes occur. In addition, they considered control algorithms that, when applied to nonlinear processes, permit operation closer to the steady-state economic optimum, even when near or within complex regimes. Their paper argued for the coordination of design, operations, and control optimizations to reduce the instances of overdesign.

Since then, considerable progress has been made in identifying processes for which design near or within complex regimes is advantageous or, if not advantageous, difficult to avoid. In this paper, reaction, separation, and mixing processes are examined. For exothermic reaction systems, an algorithm to identify those systems for which this is more profitable has been under development and is introduced briefly.

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Before beginning, it is important to acknowledge that a rapidly growing literature is evolving in the area of nonlinear control. This paper is intended to focus on process design, especially those designs that either benefit, or have difficulty avoiding, operation within or near regions having complex nonlinearities. It tends to draw upon the author's work in the reactor and distillation areas, bringing in aspects of mixing with which he is less familiar. Furthermore, it addresses some issues in the control of nonlinear systems in regions having complex nonlinearities. Three articles on the nonlinear control of chemical processes by Bequette and coworkers (1991, 1993, 1996) provided comprehensive reviews, but are no longer current. Articles have appeared since then that emphasize nonlinear predictive control (e.g., Ricker and Lee, 1995) and input/output linearizations (e.g., Soroush and Soroush, 1997).

2   Polymerization Reactors

Polymerization reactors involve initialization, propagation, and termination reactions, a large array of exothermic reactions. Often they are carried out in large batch reactors which are temperature and viscosity controlled to achieve a desirable molecular-weight distribution. These reactors must be charged, brought up to temperature gradually, and emptied in a product-removal phase. Productivity is hampered by the times to charge, to achieve an acceptable temperature level, and for product removal. Yet, given the uncertainty in the reaction rates and the molecular-weight distribution, with associated safety and environmental concerns, many processes are designed conservatively; that is, overdesigned to operate in batch mode.

Continuous operation in a CSTR is commonly more profitable. However, operation in a CSTR involves the heat-generation and heat-removal curves in Figure 1.1. Typically, these exhibit three steady states at their points of intersection. Operation at the high-temperature steady state would be most desirable, but not feasible because the rates of reaction are too high, producing a molecular-weight distribution that is too high; that is, a viscous gel that sets up like a solid phase. At the other extreme, the rates of reaction at the low-temperature steady state are too low, resulting in very large residence times and reactor volumes to achieve a satisfactory molecular-weight distribution. The intermediate-temperature steady state requires considerably less residence time and reactor volume. However, this steady state cannot be achieved without a controller because it is open-loop unstable.
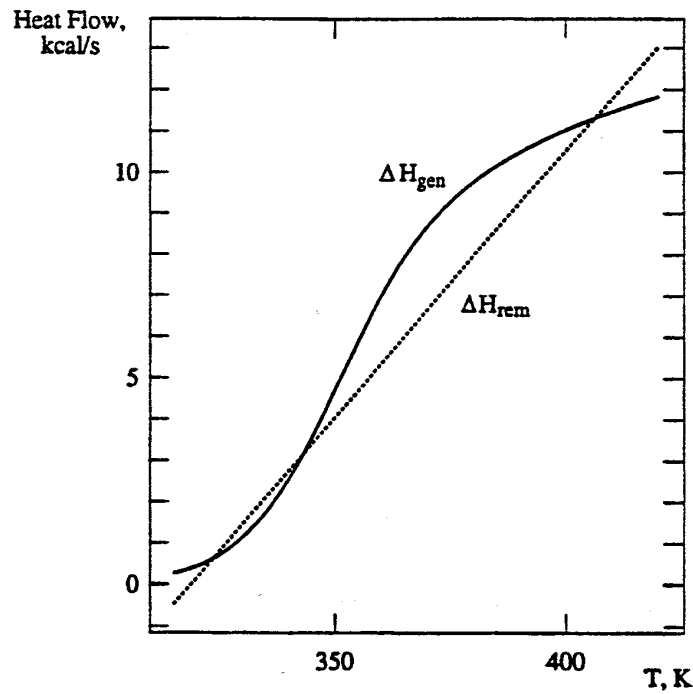
Figure 1.1   Heat generation and removal in a CSTR

Given a range of uncertainty in the expressions for the rate constants, exemplified by the upper and lower bounds in Figure 1.2, the challenge is to design a reactor and control system that can operate at this steady state while rejecting typical disturbances, such as changes in the feed temperature and the overall heat-transfer coefficient. Such a design was achieved by Gazi and coworkers (1996a) for the polymerization of styrene. In their paper, a Monte-Carlo technique is utilized to simulate the reactor and its control system for a full-range of uncertainties and disturbances. Then, in a related paper (Gazi et al., 1996b), a verification technique is introduced to confirm that the desired outputs are properly bounded throughout the Monte-Carlo analysis. With this analysis, it seems clear that the designer can examine increasingly conservative uncertainty descriptions to locate the boundaries at which the desired outputs cannot be achieved. When these uncertainties are judged to be sizable, the continuous design can be rejected.
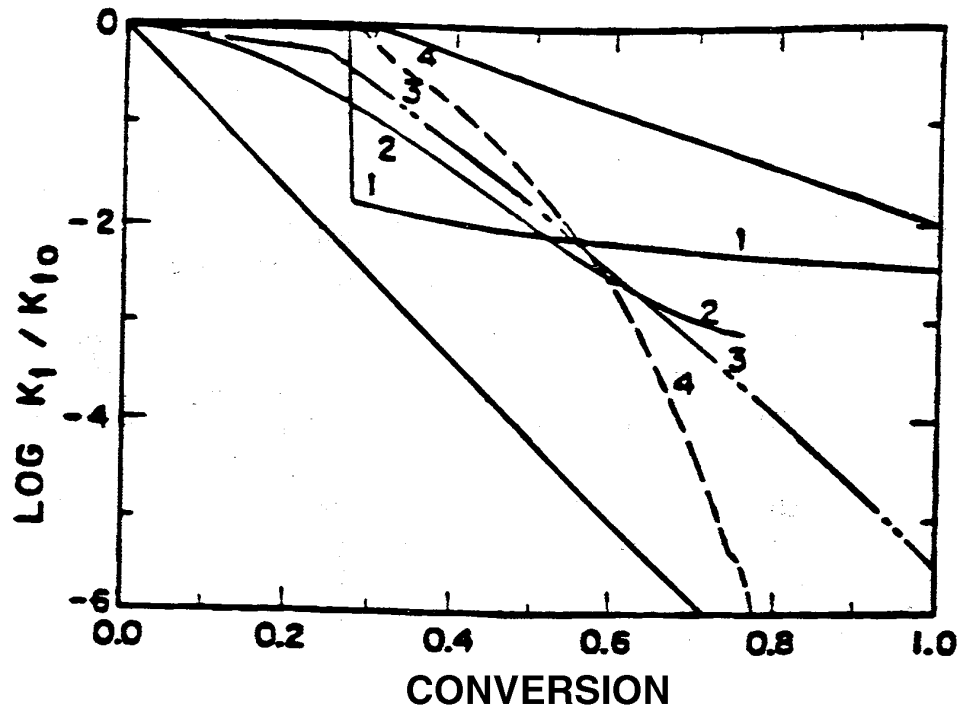
Figure 1.2   Termination rate constants for the bulk polymerization of methyl methacrylate at 70°C showing the gel effect [(1) Cardenas and O'Driscoll, 1976; (2) Friis and Hamielec (1976); (3) Ross and Lawrence, 1976; (4) Marten and Hamielec, 1979].   Reprinted with permission from Schmidt and Ray (1981).   Rate constants are nearly identical for styrene.   Bounding envelopes have been added to enclose all monotonically decreasing functions.

In another study, Lewin and Bogle (1996) examine the polymerization of methyl-methacrylate in a CSTR. To select operating points, they minimize the flow rate of the expensive initiator, while constraining the average molecular weight not to exceed 25,000. This results in two stable operating points at low-temperature steady states. Each of these operating points is examined to determine the ease of rejecting disturbances in the monomer concentration and temperature of the feed. The design that gives the smallest *disturbance costs*, that is, the smallest acceptable adjustments in the manipulated variables to achieve *perfect* control, is selected. For a complete discussion of disturbance costs, see Seider and coworkers (1999; Chapter 13).   Then, a dynamic simulation, using the nonlinear process model, confirms that this design is preferable. While the two steady states are stable, this analysis is of interest because they are in the region of multiple steady
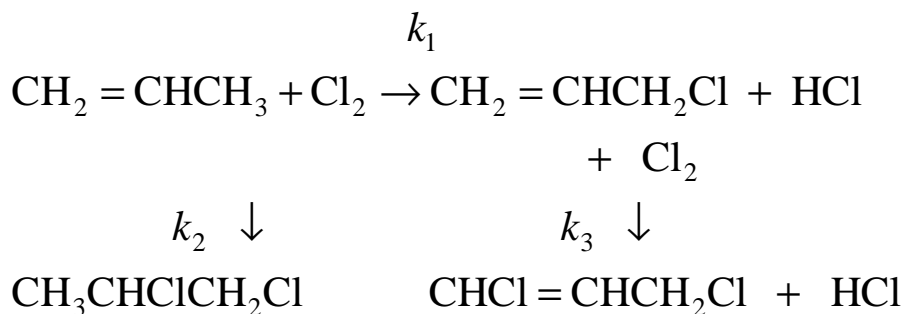
states where significant disturbances can cause the process to move from one steady state to another.

Yet another study by Teymour and Ray (1992) shows the design for a reactor to polymerize vinyl acetate that operates at a limit cycle. These authors show experimentally and theoretically, using a free-radical reaction model, that a Hopf bifurcation point is encountered as the residence time is increased. Over a sizable range of residence times, limit cycles are encountered before the periodic branch is terminated at a second Hopf bifurcation point. While the existence of periodic behavior is noteworthy, and had not been previously demonstrated experimentally, this paper does not offer compelling reasons for operating in this regime. One alternative, operation at an unstable steady state, should not be difficult to achieve with a feedback control system. Such operation has the advantage of avoiding peaks and valleys in the temperature and associated rates of reaction.

3   Exothermic Reactors

Even for reactors that don't involve polymerization, operation at intermediate temperatures can lead to higher selectivity to the desired chemicals. To achieve an intermediate temperature, at an unstable steady state, backmixing is necessary which can be achieved in a CSTR or a fluidized-bed reactor. In many designs, however, operation is in batch mode or in a tubular reactor, designed to reduce backmixing. For exothermic reaction systems, these often require more volume than a CSTR to achieve comparable conversions. Furthermore, heat removal from tubular reactors often requires additional volume and equipment as compared with CSTRs or fluidized beds.

In their initial studies, Seider and coworkers (1990) showed the potential advantage of operating a backmixed reactor, as compared with a conventional tubular reactor, for the production of allyl chloride according to the reactions:

$$CH_2 = CHCH_3 + Cl_2 \xrightarrow{k_1} CH_2 = CHCH_2Cl \; + \; HCl$$
$$+ \; Cl_2$$

$$CH_3CHClCH_2Cl \qquad\qquad CHCl = CHCH_2Cl \; + \; HCl$$

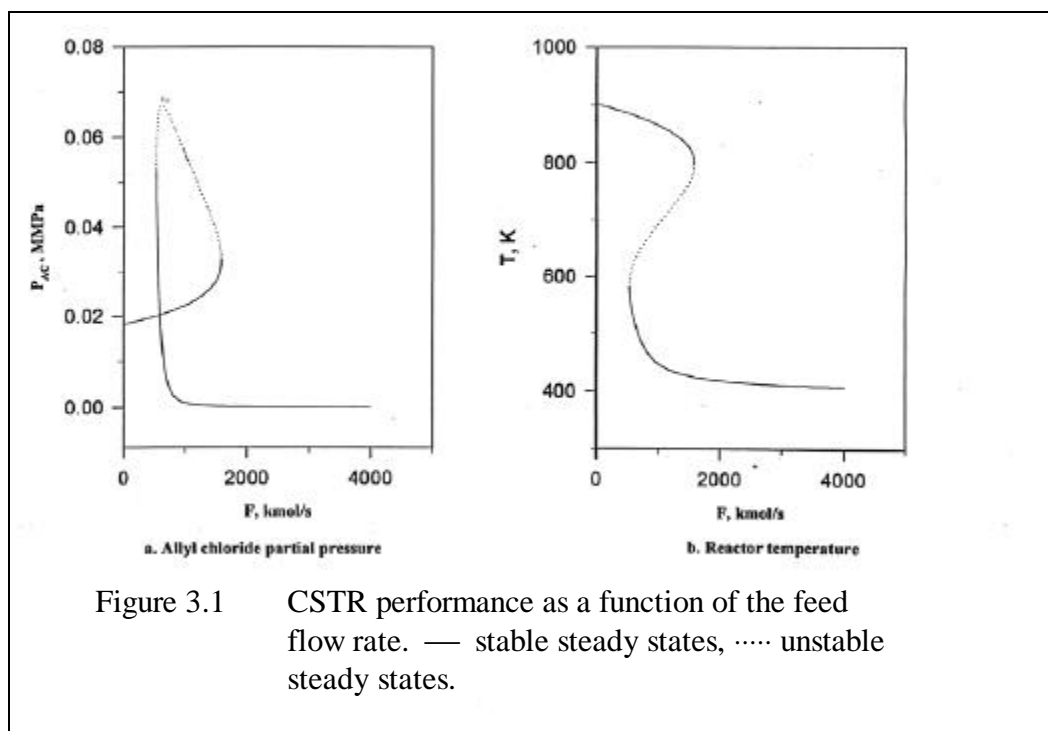with $k_2 \downarrow$ and $k_3 \downarrow$ denoting the downward reaction paths.

All three reactions are exothermic, have second-order kinetics, and exhibit an Arrhenius dependence on temperature. Both parallel and series reactions are exhibited with the desired product as the intermediate. Rate constants and heats of reaction are provided in Table 3.1.

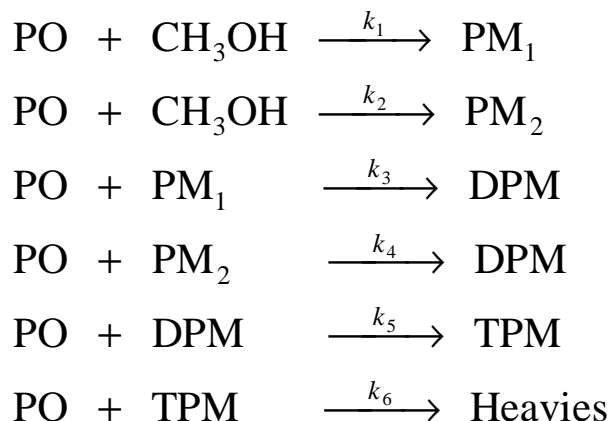| Reaction	ΔH_R Btu/lbmole	k_o lbmole/hrft^{3}atm^2	E/R °R
1	-4,800	206,000	13,600
2	-79,200	11.7	3,430
3	-91,800	4.6×10^8	21,300

Table 3.1   Rate constants and heats of reaction for the
allyl chloride reactions (Biegler and Hughes, 1983)

For this system, in a CSTR, Wilson (1996) shows that at a propylene/chlorine ratio of 1.5 in the feed, at 1 MMPa, and at a feed temperature of 400 K, the partial pressure of allyl chloride is maximized at an unstable steady state with an intermediate temperature of 650 K, as shown in Figure 3.1.

a. Allyl chloride partial pressure   b. Reactor temperature

Figure 3.1   CSTR performance as a function of the feed
flow rate. —— stable steady states, ····· unstable
steady states.

Wilson (1996) compared two process designs, one using a PFTR, and the other operating at the unstable steady state. The latter was found to be more optimal, but could not be controlled easily at the unstable steady states due to exceedingly-high rates of reaction.

Wilson (1996) also examined the reaction of propylene oxide with methanol which reacts in a sequence of exothermic parallel and series reactions in the presence of KOH or NaOH catalyst:

$$PO \; + \; CH_3OH \; \xrightarrow{\;k_1\;} \; PM_1$$

$$PO \; + \; CH_3OH \; \xrightarrow{\;k_2\;} \; PM_2$$

$$PO \; + \; PM_1 \; \xrightarrow{\;k_3\;} \; DPM$$

$$PO \; + \; PM_2 \; \xrightarrow{\;k_4\;} \; DPM$$

$$PO \; + \; DPM \; \xrightarrow{\;k_5\;} \; TPM$$

$$PO \; + \; TPM \; \xrightarrow{\;k_6\;} \; Heavies$$

where PM_1 and PM_2 are the primary and secondary isomers of mono-propylene-glycol-ether, and DPM, TPM, and heavies represent the di, tri, and heavy propylene-glycol-ethers. Again, the selectivity to the desired product, PM_1, was shown to be highest at an unstable steady state having an intermediate temperature. However, in this case, the increase in selectively, as compared with operation in a process with PFTRs, was offset somewhat by the decreased conversion in the reactor and the need to recirculate more unreacted propylene oxide and methanol.

Wilson (1996) attempted to create an algorithm to identify exothermic reaction systems for which operation at an unstable steady state, to achieve increased selectivity and higher profits, is advantageous. Thus far, the entire algorithm has been evaluated for only two systems, for the production of allyl chloride and propylene-glycol-ether, with only moderate success recorded for the latter. Yet, for exothermic parallel-series reaction systems:

$$A \; \xrightarrow{\;1\;} \; B \; \xrightarrow{\;3\;} \; D \; \longrightarrow \; E \; \longrightarrow \; F$$
$$A \; \xrightarrow{\;2\;} \; C \; \xrightarrow{\;4\;} \; D$$
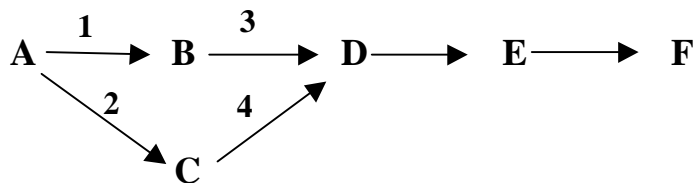
in which species B is the desired product, it seems clear that selectivity to species B is increased at intermediate temperatures when:

$$E_1/E_i > 1 \qquad i = 2, 3, 4$$

When this test is passed, the proposed algorithm examines the pre-exponential factors to estimate the rates of the reactions, and separation factors (such as relative volatilities) to estimate the difficulty of separating the unreacted species from the products. Then, operating points are selected, using homotopy-continuation analyses, and design optimization and control studies are carried out.

4   Distillation Towers

In distillation towers, multiple steady states have been predicted using various models that assume phase equilibrium for over a decade. Only recently, have experimental data been reported to confirm these predictions.

Since intuition anticipates that this nonlinear behavior is associated with non-ideal mixtures, it is especially noteworthy that Jacobsen and Skogestad (1991) computed multiple steady states for the separation of methanol and propanol, a nearly-ideal mixture. Their study shows that hysteresis behavior occurs when the mass flow rate of the reflux is varied rather than the molar flow rate. Since the mass flow rate varies linearly as the stem of the reflux valve is adjusted, the mass flow rate is the appropriate independent variable. Consequently, the nonlinear relationship between the mass and molar flow rates results in turning points and multiple steady states.

For homogeneous azeotropic mixtures, probably the first experimental confirmation of multiple steady states was reported by Guttinger and coworkers (1997) for the ternary mixture, methanol-methyl butyrate-toluene. Three solution branches are computed over a range of distillate flow rates using equilibrium-based models, with the two stable steady-state solutions confirmed using experimental measurements in a packed tower. Hence, for this system, at least, the composition measurements are not a strong function of the extent of mass transfer. Also, since the calculations using the AUTO program assume constant molal overflow, heat effects are small of this mixture. Subsequently, in an experimental study involving methanol-methyl butyrate-toluene, Dorn and coworkers (1998) use a simple PI-controller to stabilize the intermediate steady states along the open-loop unstable branch. This is followed by a theoretical study for the same ternary mixture in which Lee and coworkers (1999) use the AUTO program (Doedel and Wang, 1994) to show the existence of Hopf bifurcations and periodic cycling. While there is no experimental verification, incidences of periodic motion in experiments in laboratory towers are reported, providing justification for the consideration of periodic motion and searches for this behavior in future experiments.

Probably the first comprehensive, theoretical discussion of multiple steady states in the distillation of heterogeneous azeotropic mixtures was provided by Bekiaris and coworkers (1996). These authors showed how to vary the distillate flow rate to locate multiple steady states for towers in the limits of infinite reflux and an infinite number of trays. The existence of multiple steady states is shown to be relevant for towers having finite reflux and trays. The effectiveness of their analysis is illustrated for towers that dehydrate ethanol with benzene entrainer.

More recently, Muller and Marquardt (1997) verified the existence of multiple steady states in a small laboratory tower, having just eight trays, for the ethanol-water-cyclohexane mixture. In calculations, using a model that assumes an infinite number of

stages and an infinite reflux ratio, as well as a model that solves the MESH equations without assumptions, a region of three steady states is computed as the distillate flow rate is varied. Measurements for the two stable steady states are in close agreement with the calculations. However, measurements could not be made for the unstable steady state due to limitations in the decanter residence time for the operating conditions selected. In another study, Wang and coworkers (1997) measured the existence of two of the three steady states in a laboratory tower for the isopropanol-water-cyclohexane mixture. Finally, in a theoretical study, Esbjerg and coworkers (1998) examine two sequences for the dehydration of ethanol using cyclohexane, involving distillation columns to recover ethanol and water. While multiple steady states are computed for each sequence, the order of the columns and the position of the decanter are shown to influence the nature of the steady-state solutions.

For distillation towers involving mixtures that can form two liquid phases, there are advantages in removing a second liquid phase as a side product, especially for mixtures of oxygenated hydrocarbons and water, where water is an intermediate-boiling species. Ciric and coworkers (1999) present results for a tower with an internal decanter in which five oxygenated hydrocarbons (A, B, C, D, and E) and water are separated. The mixture contains two partially-miscible binary pairs, C-water and B-C. Calculations using an equilibrium-based model in ASPEN PLUS are confirmed using experimental measurements under normal operation. However, a second steady-state solution is computed in which two liquid phases are displaced away from the decanter tray. Furthermore, in a different regime, having low bottoms flow rates, two steady-states are computed, with and without two organic liquid phases on the decanter tray. While these incidences of multiple steady states are not confirmed experimentally, it seems clear that their potential existence should be considered in process design and control.

Heterogeneous distillations, of the type described above, need special attention when selecting the methods for estimating the liquid activity coefficients in vapor-liquid-liquid equilibria. Furthermore, methods for assessing both the thermodynamic stability of phase distributions and the dynamic stability of the processes, as the process moves in response to disturbances, must be carefully selected. These methods are discussed by Widagdo and coworkers (1992) and Widagdo and Seider (1996).

In summary, like polymerization reactors, exothermic reactors, and mixing devices, for some mixtures, distillation towers operate near or within regions having multiple steady states. It is especially noteworthy, however that, in my opinion, no advantages have been demonstrated for operation at unstable steady states and at limit cycles. Furthermore, unlike polymerization and exothermic reactors, distillation columns are relatively easy to control, even at open-loop unstable steady states, as shown experimentally by Dorn and coworkers (1998). This is because the large holdups on the trays and, especially, in the sump, reflux accumulator, and decanter, cause the time constants to be relatively large, on the order of minutes and hours. For this reason, simple controllers can be used to prevent slow movement from one steady state to another or a transition into periodic motion.

5   Mixing

In fluid mixing, a high degree of disorder is desirable.   Stated differently, in a review article, "Fluid mixing is an instance in which chaos is clearly beneficial" (Ottino et al., 1992). Furthermore, their review article identifies streamline crossing as a necessary condition for chaos in fluid flows which, when combined with stretching and folding, results in effective mixing within chaotic regions. This is accomplished through suitably designed time-periodic flows, with time modulation achieved by out-of-phase boundaries, increased Rayleigh number (in Rayleigh-Benard flows), increased Reynolds number, vortex shedding behind a cylinder, among other mechanisms.

At low Reynolds numbers, where creeping flow prevails, viscosities are high and flows are laminar. Special mixing devices, including extruders, are designed to achieve effective mixing while consuming a minimum amount of energy. Ottino and coworkers (1992) indicate that engineers seek to select desirable impeller sizes and geometries, optimum sequences of elements for static mixers, or optimum placements of pins in extruder channels. Furthermore, by considering the symmetry of flows, the problem can be reduced to a more tractable one because symmetry in chaotic flows is related to the geometric constraints on the fluid motion; that is, symmetry can be used to develop rules for the geometric arrangements of elements in a static mixer, or the placement of baffles in a channel or tank.

More specifically, in slow flows within a rectangular cavity with fixed vertical walls ($Re \leq 1$), chaos is generated by alternatively moving the top and bottom walls with constant velocity, each for a time $T/2$, where T is the non-dimensional period of the flow (defined as the total displacement of both walls during one cycle, divided by the length of the cavity). Such a *cavity mixer* is shown schematically in Figure 5.1 Liu and coworkers (1994) simulate the existence of the time-periodic flows and confirm that agreement is obtained with the experimental measurements of Leong and Ottino (1989).
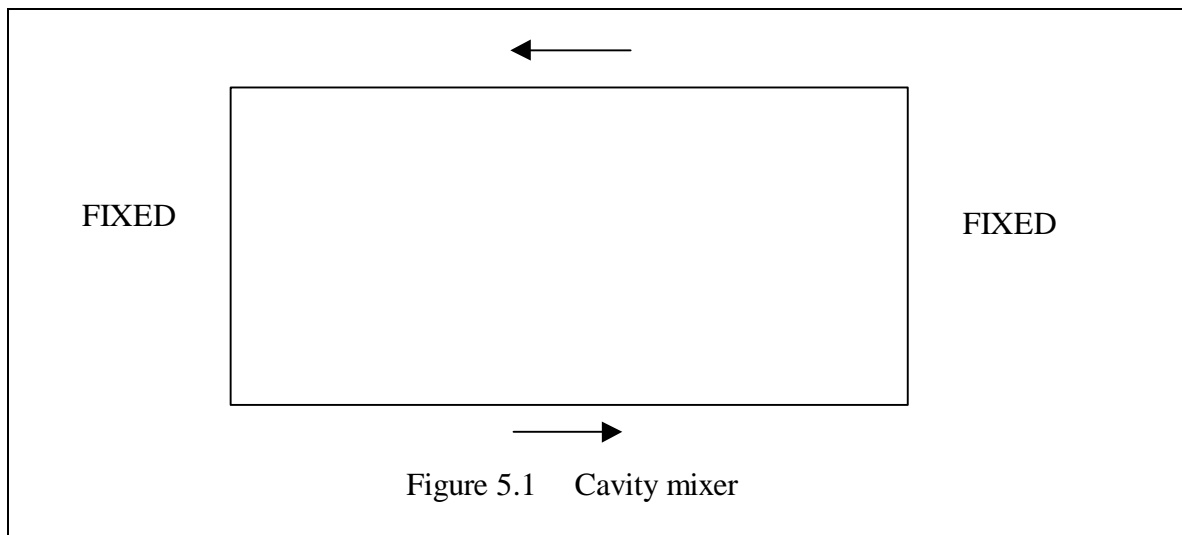

Figure 5.1   Cavity mixer

The Kenics mixer, a static mixer shown in Figure 5.2, is also designed for slow flows. Using computational fluid mechanics (CFD), Hobbs and Muzzio (1997) examine its performance for mixing small streams into a bulk flow as a function of the injection location and the flow ratio.
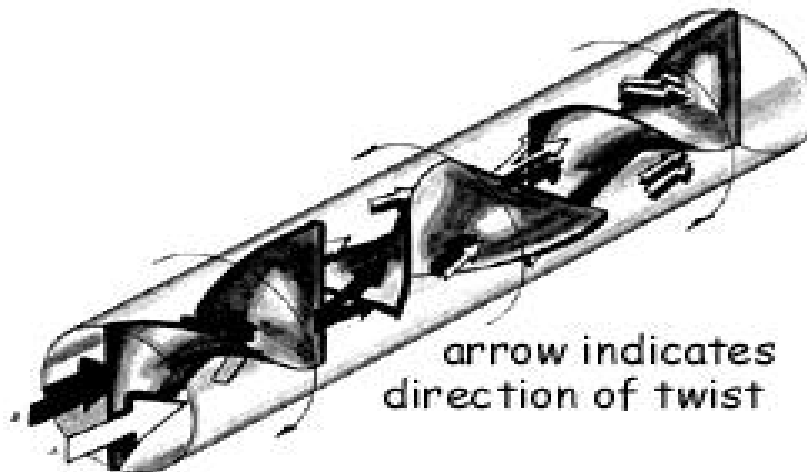
Figure 5.2   Idealized view of Kenics static mixer. Two streams, A and B, enter segregated. After the first twist (clockwise), each stream is halved and joined by half of the other stream in the second twist (counte-clockwise). This process is repeated periodically. Reproduced from Ottino (1989) with permission.

For these and similar mixers, involving slow flows, the degree of chaos or mixing is not easily measured online, and consequently, feedback control systems are not used. Other mixing devices, however, intended to obtain uniform temperatures and concentrations, for higher speed flows, are controlled by varying the agitator speed in a feedback control loop. In these cases, the degree of mixing, or chaos, is approximately a function of the radial temperature and concentration distributions.

In processes that are heated from below and cooled from above, the mechanism of natural convection can often be controlled by adjusting the heating rate in a feedback control loop. This has been demonstrated experimentally and theoretically by Wang and coworkers (1992) for the toroidal thermal-convection loop shown in Figure 5.3. Their paper shows how a feedback controller can be used to suppress (laminarize) the natural convection or induce chaos in otherwise time-independent flows. The control strategy consists of sensing the deviation of fluid temperatures from set points at several locations

inside the tube and altering the heating rates to either counteract or enhance such deviations.

Figure 5.3   Schematic of a toriodal thermal convection loop.
Reprinted from Wang et al. (1992) with permission.
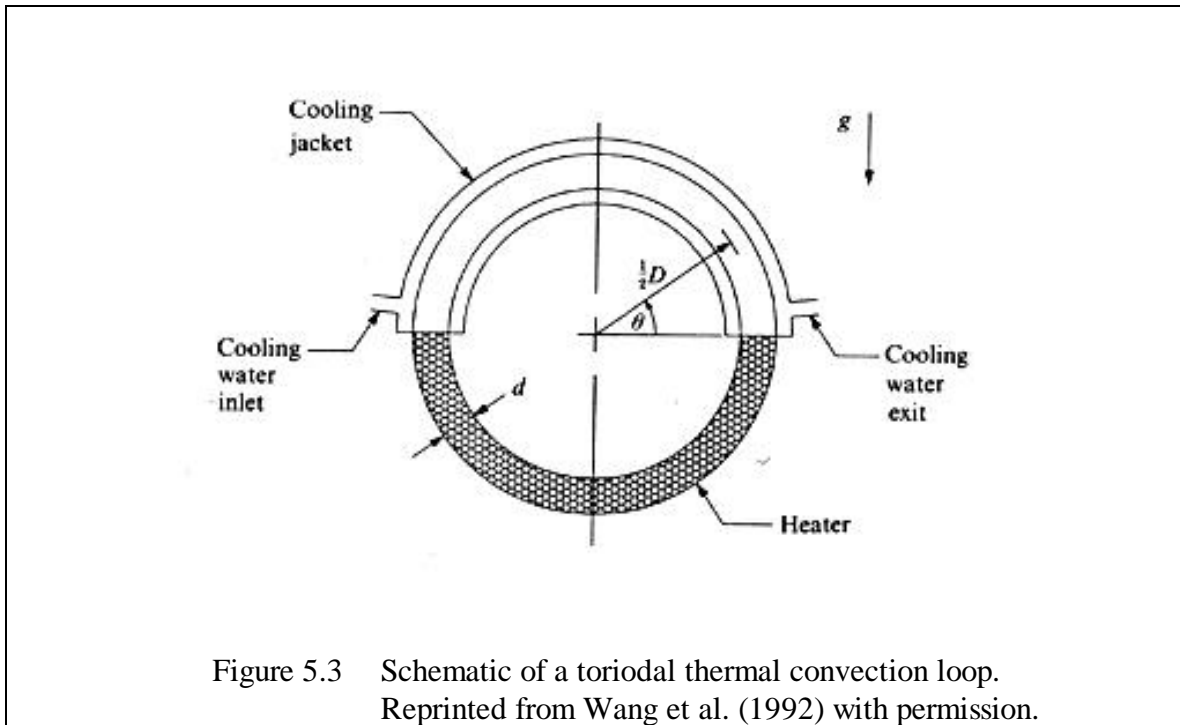
6   Design and Control Optimization

In design, an objective function subject to constraints is optimized by adjusting the degrees of freedom available. Similarly, in process control, the objective is often to minimize a performance measure which indicates the proximity of the responses to typical disturbances to the desired set points. In principle, as the design objective moves closer to or within regimes of complex nonlinearity and/or closer to operating constraints, the performance measures increase as it becomes more difficult to track set point changes and reject disturbances. Almost 10 years ago, we provided a general formulation for a coordinated design and control optimization (Brengel and Seider, 1992), and applied it with moderate success to the design of a fermentation reactor and its control system at an open-loop unstable steady state.

Coordinated optimizations are difficult to formulate and solve, and consequently, attempts have been made to assess the controllability and resiliency of a potential process using more approximate measures such as *relative gains* and *disturbance costs*. These permit the controllability and resiliency of a potential design to be evaluated without the need to design and tune the individual control loops. Stated differently, it is acceptable to assume perfect operation of the control loops in carrying out this evaluation. The first measure often provides a fine indication of the interaction between control loops when set point changes are experienced. As discussed by Seider and coworkers (Chapter 13, 1999), pairings between manipulated and controlled variables are selected on the basis of

the proximity of the relative gains to unity. Similarly, disturbance costs indicate the extent to which the manipulated variables change when disturbances are encountered. Here, the most easily controlled process designs, when selecting from alternatives, are expected to be those that keep all of the manipulated variables from having large changes. While these measures are approximate in that they are applied to systems linearized about a steady state, they are very helpful in the preliminary stages of process design when it is important to reject processes that are projected to be difficult to control.

Luyben and Floudas (1994a,b) introduce a formulation that computes process gains at each steady state as the design optimization proceeds. A condition number is computed to assess the difficulty of controlling each process design during the solution of a mixed-integer nonlinear program (MINLP). Perkins and Walsh (1996) discuss this formulation and others, mostly based upon the work of Perkins and colleagues, in which optimization methods are utilized to select control structures during process synthesis and to select process and control structures that satisfy dynamic performance objectives.

Finally, when seeking methods to solve efficiently these combined optimization problems, it is important not to lose sight of several important steps in designing a *plant-wide control* system. These are elucidated by Luyben and coworkers (1998) who recommend a 9-step design procedure including:

> "Establish the energy management system. Make sure that energy disturbances do not propagate throughout the process by transferring the variability to the plant utility system.
>
> Set the production rate. Establish the variables that dominate the productivity of the reactor and determine the most appropriate manipulator to control production rate.
>
> Fix a flow in every recycle loop and control inventories (pressures and levels)."

When developing optimization strategies, steps such as these need to be incorporated, possibly in creating the superstructure, the objective function, and/or the constraints. In the immediate future, hybrid approaches are likely in which these steps are carried out before or during the solution of various optimization problems.

7   Conclusions

It is concluded that:

1.   Polymerization reactors are prime candidates for operation at an unstable steady state, with many incidences reported in industry. While periodic

behavior has been measured experimentally in a CSTR, there doesn't appear to be an advantage to such operation, as compared with control at an unstable steady state. Continuous operation appears to increase production, compared with batch operation.

2. It can be advantageous to operate an exothermic reactor at an unstable steady state when it involves competing reactions in parallel and series. Selectivity to the desired chemical can be increased at an intermediate temperature when the activation energy of the reaction(s) that produces the desired chemical is smaller than that for the competing reactions. The broad outline of an algorithm to screen reaction systems for more selective operation is introduced herein.

3. Distillation towers often exhibit multiple steady states, even when near-ideal mixtures are being separated. Thus far, no advantage to operating at an unstable steady state appears to have been identified. Furthermore, there appears to be little difficulty controlling distillation towers in or near regions that exhibit multiple steady states. This is because of the large holdups that cause the response times to typical unanticipated disturbances to be quite large.

4. In mixing operations, it is very desirable to operate in a chaotic mode. Controllers are not normally utilized for polymer mixers because of the difficulty in measuring the degree of mixing. In other mixers, the agitation rate is often a fine control variable.

5. When coordinating design and control optimizations, approximate measures for screening on the basis of controllability and resiliency are being formulated to enable their assessment during design optimization.

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