REACTOR DESIGN FROM A STABILITY VIEWPOINT

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IT MIGHT, IN ALL fairness, be asked what it is in the subject of Chemical Reactor Design that provides the central themes. On what basis, for example, does one decide to include one topic and exclude another? Are the subjects of mixing and residence time distributions pertinent and important? They are in essence physical effects rather than chemical, and could as well be presented in a context of transport processes. If utilitarian needs are to provide the distinctions, one might move to include selective material on multiphase reactions, but such models are rather complicated and still distant from practical use. The decisions are often a reflection of the textbook and expertise that happen to be available. Under the circumstances, with a vast range of topics to choose from, the dependence on an available expert may in fact be a fine basis for choice, even if a bit arbitrary in nature.

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One might focus on the same question from another viewpoint. Should one not expect growth and development from the subject matter in a course? If the material of later weeks is interchangeable in sequence with that of the early weeks in the series and does not build upon it as a requisite, if there is no unifying theme, then is there a legitimate basis for claiming that the series of lectures form a single course? A similiar point could be made in categorizing a textbook (or for that matter, any book). It is often an excellent idea to publish an anthology or a collection of short stories, but no one would call such a book a novel.

The graduate reactor design course at the University of Pennsylvania uses stability as a central theme around which to organize a wide range of reactor concerns. This approach brings together the subject matter of catalyst particles with that on well-stirred vessels and tubular reactor geometry. It emphasized the similarities among the diverse models rather than their differences. It does, however, make distinctions between lumped and distributed models, between algebraic and differential equation models, and among the assumptions that are commonly made in arriving at numerical solutions from each starting point. The course is built around the author's textbook called "Stability of Chemical Reactors" (Prentice-Hall, 1972).

Of the term stability, Richard Bellman has said that it has an unstable definition. In the ChE literature, for example, it has been used to mean steady state multiplicity, as well as parametric sensitivity. Even in its closer-to-mathematical sense, the term has been used to refer to local behavior (in the "neighborhood") about a steady state, and to trajectory motion in a large region of state space. The clarification of such ambiguity is an early objective of this course. It is handled by means of a variety of examples that illustrate the need for rigorous definitions. A detailed course outline is presented as Table 1.

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TABLE 1
Chemical Reactor Design Course Outline

- I. INTRODUCTION
  - A. What is reactor design: objectives and justification
  - B. Stability approach as a unifying theme
- II. REVIEW OF BASICS
  - A. Nomenclature, CSTR equations, special cases
  - B. Volume and density changes
  - C. Unsteady state behavior
  - D. Batch reactor quadratures
  - E. Kinetics review: mechanisms and rate equations
- III. MULTIPLICITY AND STABILITY
  - A. Various definitions of stability
  - B. Uniqueness in an isothermal CSTR
  - C. Local stability criteria
  - D. Two-equation models
  - E. Is uniqueness good? Design questions.
  - F. Temperature variation
  - G. Techniques for simultaneous equations
- IV. PHASE-PLANE ANALYSIS OF THE CSTR
  - A. Trajectories, isoclines, eigenvectors
  - B. Feedback control
  - C. Regions of stability
  - D. Liapunov stability
  - E. Gerschgorin's theorem
  - F. Practical stability
  - G. Tracking function graphical technique
- V. TUBULAR REACTORS
  - A. Plug flow model, isothermal
  - B. Volume comparisons to CSTR
  - C. Simultaneous and sequential reaction
  - D. Staged reaction and cold-shot cooling
  - E. Maintenance and cooling considerations
  - F. Parametric sensitivity: Barkelew's correlation
  - G. Steady state operating curves
  - H. Adiabatic reactors
  - I. Harriot's and Wilson's Rules for cooling capacity
  - J. Effect on recycle on PFTR: multiplicity and stability criteria
- VI. DISPERSION EFFECTS
  - A. Characterization of dispersion in a tube
  - B. Danckwertz boundary conditions
  - C. Special cases of axial or radial dispersion
- VII. CATALYST PARTICLES
  - A. Effectiveness factors
  - B. Experimental tests
  - C. Multiple profiles and stability
  - D. Collocation technique

LUMPED MODELS

A STRAIGHTFORWARD ANALYSIS of the isothermal CSTR provides a vehicle for the development of new ideas in the context of an already familiar model. It is a surprise to some students to learn that multiple steady states can arise at all in an isothermal system. They explore this idea as an outgrowth of kinetic forms and carry the arguments to apply to free radical initiations and to chemostat biochemical models. The subject matter turns to temperature dependent energy considerations, but by this time the students have already handled the essential concepts arising from multiplicity. They learn to draw van Heerden diagrams and ignition and extinction hysteresis loops as particular cases of phenomena previously encountered in the isothermal systems.

In an analogous way, the techniques of linearization and eigenvalue analysis are introduced together with the simplest one-equation models. Local stability and regions of stability are first demonstrated for single-variable equations; they are then developed for multidimensional models,

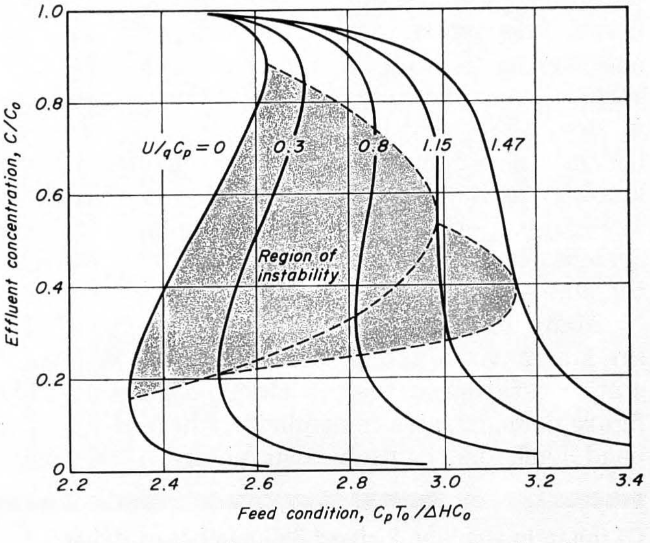

FIGURE 1. Steady-state operating curves for the temperature-dependent CSTR with region of instability.

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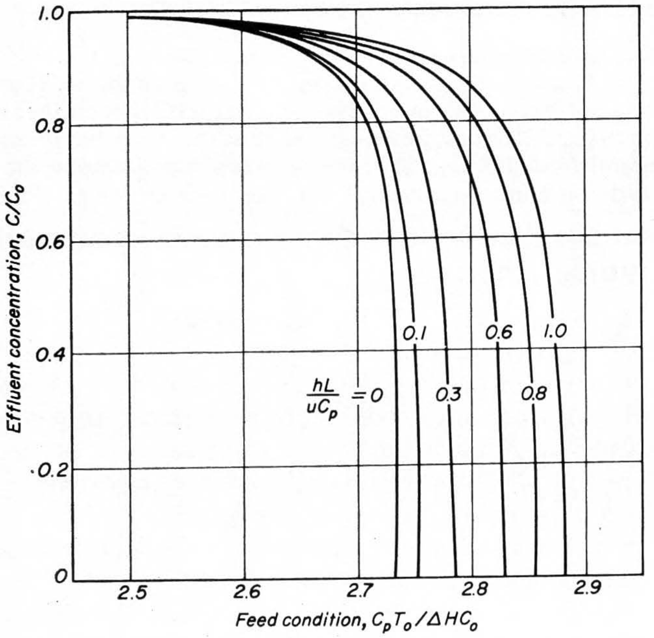

FIGURE 2. Steady-State operating curves for the PFTR.
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some including thermal effects, some with feedback control loops. This leads naturally into a review of linear algebra and phase-plane analysis. The results are used to consider trajectories during start-up, physical interpretation and eigenvectors, and direct methods for establishing stability.

Some time is devoted to Liapunov analysis in part because of its applicability to nonlinear systems, but also because it provides an excellent point of departure for questions of practicality in engineering as well as numerical analysis. This subject leads one to question the fundamental objectives of reactor design: Is multiplicity good or bad in design? Should the designer prefer a large stability region or a small one? What is a practical stability criterion? When is a Liapunov-unstable system acceptable for practical use, and when is the stable system unacceptable?

Many of the numerical results of the CSTR are summarized and presented as a set of steady state operating curves, such as Figure 1. This figure demonstrates multiplicity where the curves bend back on themselves, it shows a relatively large region in the parameter space where steady states are unstable, and it includes a range of parameter values for which a single, but unstable steady state is found (a limit cycle).

DISTRIBUTED MODELS

THE POINT OF DEPARTURE for the realm of distributed models is the observation that a plug-flow (PFTR) geometry can produce steady state profiles with great parametric sensitivity, but it does not exhibit any multiplicity or instability for a given choice of design parameters. This argument is developed in considerable detail by discussion of the well-known work of Barkelew, Harriot, and Amundson. It is shown pictorially by Figure 2, where the lack of any sigmoid-shaped curves corresponds to a lack of multiple intersections for a given feed condition.

A second major milestone in this part of the course is the connection with feedback by recycle. The technique is based on the simultaneous solution of a recycle equation of the form:

$$C_o = (1-f)\, C_F + f\, C_E \qquad (1)$$

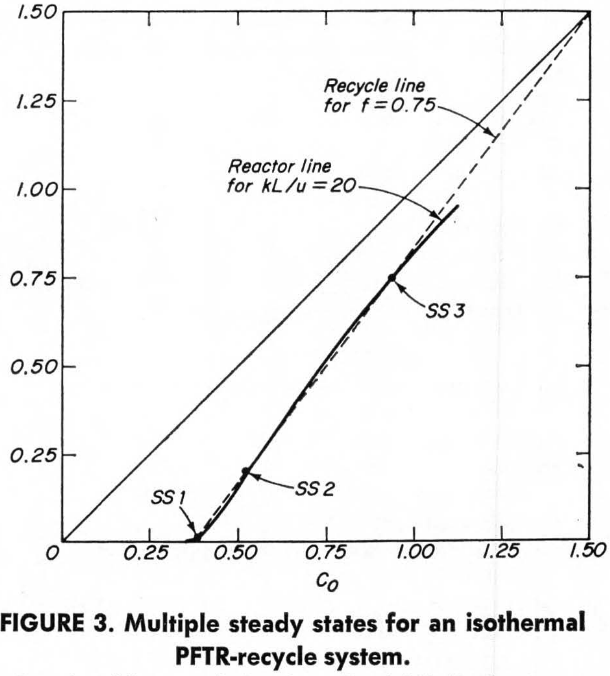

FIGURE 3. Multiple steady states for an isothermal PFTR-recycle system.
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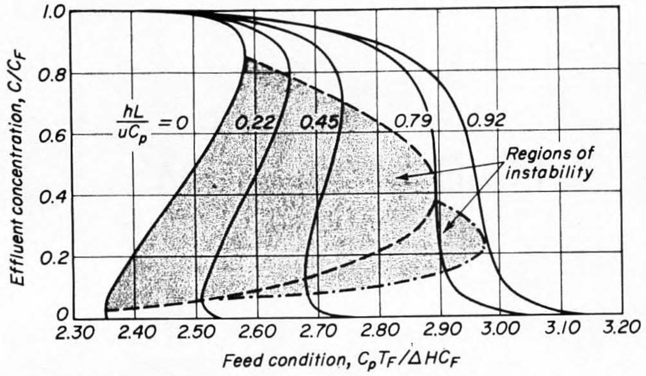

FIGURE 4. Steady-state operating curves for PFTR-recycle system with f = 0.5 (Reilly and Schmitz, 1966).

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with the PFTR isothermal mass conservation statement.

$$\frac{L}{u} = \int_{C_o}^{C_E} \frac{dC}{R} \qquad (2)$$

When the latter equation is integrated to produce an algebraic relation, the simultaneous solution is most readily obtained from intersection points on a C_E vs C_o graph.

An illustration is given in Figure 3, obtained by postulating a rate equation of the form

$$R = \frac{kC}{(1 + KC)^2} \qquad (3)$$

and choosing selected values of f, K, C_F, and the group (kL/u). The solution shows three steady state solutions (profiles in the PFTR) and very marked sensitivity to the choice of recycle rate. From a presentation of results such as Figure 3, it becomes apparent that multiplicity in these systems must be associated with recycle (or mixing), since even the isothermal PFTR reactor can show multiple steady state profiles when some of the product is appropriately recycled.

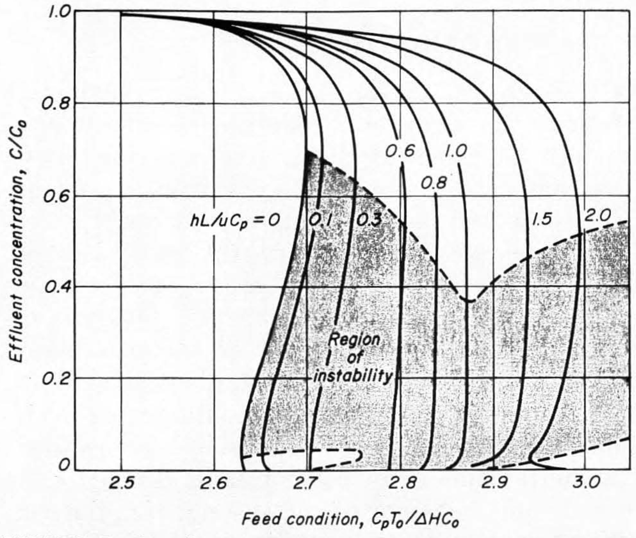

FIGURE 5. Steady-state operating curves for the TRAM [$\alpha = D$, (uL/D = 10] showing a region of instability.

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When this problem is extended to include adiabatic and then temperature-dependent changes, the recycle behavior can be described in terms of sets of finite-difference equations. The similarity to ordinary differential equations is noted as is also the major point of difference in terms of eigenvalue criteria. The results of a numerical study by Reilly and Schmitz are presented to illustrate the essential features of this system (see Figure 4).

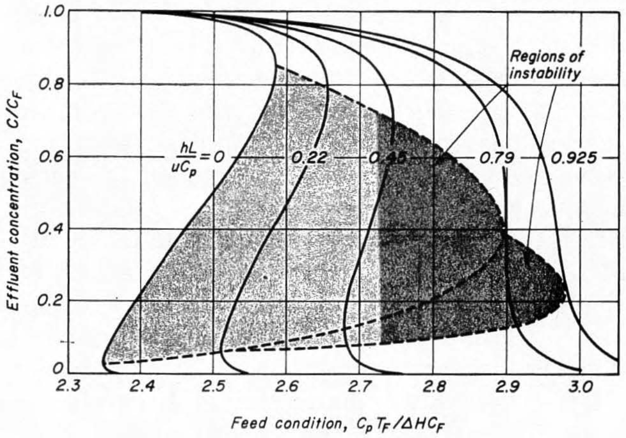

FIGURE 6. Steady-state operating curves for TRAM-recycle system with f = 0.5, uL/D = uL/α = 100.

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The consideration of tubular reactor geometry takes a more ambitious direction as dispersion effects are introduced in terms of a Peclet number and second derivative term. The need is established for new boundary conditions, and it is demonstrated that this mode of backmixing can also lead to multiplicity and instability of solutions. From this perspective the catalyst particle problem is viewed as merely a special case for which no macroscopic flow term exists.

When it is appropriate to call for numerical solutions to the distributed parameter models, they serve as a natural bridge to a presentation of the methods of weighted residuals. In particular, both

Continued on page 176

in the latter the behavior is dependent on the nature of the extraneous object or is induced by it (e.g., diffusion through a membrane).

OTHER REMARKS

GRADUATE EDUCATION EXTENDS far beyond the confines of the classroom, and that is particularly true in a course of this type. Firstly, there are no standard textbooks although a substantial portion of the material can be found in related books, monographs, and technical articles. (A list of some useful references can be obtained from me.) In addition, considerable amount of independent work and self-study is essential to keep abreast of the lecture material, and this can be encouraged through appropriate exercises and term-paper assignments (usually critiques of recent technical articles)—a not-uncommon practice in graduate-level courses. A few prerequisites, such as first-level courses in real analysis and probability theory, are desirable especially since a student unfamiliar with the mathematical notions and terminology is usually overwhelmed by the analytical techniques. Needless to say, while techniques should be available at command, they should never take precedence over the concepts.

Finally, it is not the intention of the course to create, in the words of Bertrand Russell, an ordered cosmos where pure thought can dwell remote from human passions and remote from the pitiful facts of nature. The intention certainly is not the latter, and in fact I feel that the "pitiful facts of nature" demand approaches of this type. And, more importantly, a prime objective of the course is to emphasize not the special nature of the subject matter but the synthesis of a set of diversified, yet structurally similar, classes of problems and the need and the benefits of such a synthesis.

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REACTOR DESIGN: Perlmutter

Continued from page 171

Galerkin's method and collocation techniques are introduced as a means of reducing partial differential equations to sets of simultaneous ordinary differential equations. The latter lead smoothly to the earlier lumped stability techniques, and make available the wide range of prior methods in the treatment of distributed systems.

It is pointed out that this approach can also be used to compute complete numerical solutions to the same equations, if they are needed in addition to the stability finding.

Yet another demonstration of the use of stability analysis as a unifying theme may be found in Figure 5, where results are presented for a tubular reactor with axial dispersion (TRAM). Here again, one can detect regions of multiplicity and instability introduced by the backmixing effect. If the specific parameter values are chosen differently, this pattern of behavior can be modified to approach either the CSTR or PFTR results as the dispersive effect grows or diminishes with respect to the other parameters. When a recycle stream is added to the TRAM system, it serves to reinforce the backmixing that arises from the action of dispersive flow, and the overall effect shows a great resemblance to the CSTR result. Such operating curves are presented in Figure 6 for a typical set of parameters. □

NOMENCLATURE

C = reactant concentration
C_o = reactant concentration in reactor feed
C_E = reactant concentration in reactor effluent
C_F = reactant concentration in make-up feed
C_p = heat capacity
D = dispersion coefficient
f = fraction recycled
h = heat transfer coefficient for PFTR
ΔH = heat of reaction
k = kinetic rate constant
K = kinetic rate constant
L = reactor length
q = volumetric flow rate
R = reaction rate
T_F = temperature of make-up feed
T_o = temperature of reactor feed
u = linear flow rate
U = overall heat transfer coefficient for CSTR
α = thermal dispersion coefficient