New Stability Analysis Based on Iterative Sampling and Optimization

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Mathematical models of chemical reactors are known to exhibit complex bifurcation behavior due to the strong coupling between transport processes and the reaction kinetics, which depend in a nonlinear way on temperature and concentration. Several sophisticated programs enable the tracking of different bifurcation points of various codimension, such as AUTO (Doedel et al., 1997) or CONTENT (Kuznetsov et al., 1996). These codes, however, are practical only for reactor models of low to intermediate complexity. Mathematical models of chemical reactors are commonly written as

$$\boldsymbol{C}(\boldsymbol{U},\boldsymbol{p})\cdot\frac{d\boldsymbol{U}}{dt}=\boldsymbol{F}\left(\boldsymbol{U},\nabla\boldsymbol{U},\nabla^2\boldsymbol{U},\boldsymbol{p},t,\tau\right)=\boldsymbol{0} \qquad (1)$$

with the corresponding boundary and initial conditions. $\boldsymbol{U}$ is a state vector, $\boldsymbol{C}$ is a capacitance matrix, $\boldsymbol{F}$ is a vector of nonlinear functions, τ is the forcing period in case the reactor is periodically forced, and $\boldsymbol{p}$ is the set of parameters (reactor dimensions, feed rates, and so on). In practice, it is important to know the impact of changes in the operating conditions (parameters) on the various states of the reactor. Different attractors exist and, depending on the initial conditions, the reactor will approach one of the stable attractors. Examples are single, or multiple steady states, and periodic, quasi-periodic, or chaotic oscillations (Parker and Chua, 1989). The dependence of the reactor state on the operating conditions is usually presented in the form of *bifurcation diagrams*. We define two bifurcation diagrams to be *qualitatively similar* when the number, order, and orientation of the solutions $\boldsymbol{U}$ change in an identical way upon a continuous change in a parameter $P \in \boldsymbol{p}$.

The boundaries of parameter regions with qualitatively similar bifurcation diagrams may be determined by application of the singularity theory with a distinguished parameter developed by Golubitsky and Schaeffer (1985). They proved that, next to an organizing center (highest-order singularity), the qualitative features of the local bifurcation diagrams of the universal unfolding of $\boldsymbol{F}(\boldsymbol{U},\boldsymbol{p})=\boldsymbol{0}$ may change only if the parameter set crosses one of three hyper-surfaces in the parameter space of the unfolding parameters: *hysteresis*, *double limit*, and *isola* variety. Typically, two limit points coalesce upon crossing the hysteresis variety, while an isolated branch of solutions appears (or disappears) upon crossing the isola variety. Crossing of either the hysteresis or isola variety typically changes by two the number of limit points of the bifurcation diagrams. Crossing a double limit variety typically changes the relative positions of two limit points in the bifurcation diagrams. Uppal et al. (1974, 1976) used bifurcation analysis to map the dynamic features of the CSTR. Balakotaiah and Luss (1983, 1984, 1988) used the three varieties to divide the global parameter space of lumped reactor models into regions with qualitatively different bifurcation diagrams. For distributed reactor models, $\boldsymbol{F}(\boldsymbol{U},\boldsymbol{p})=\boldsymbol{0}$ is a boundary value problem in one to three spatial dimensions. Jensen and Ray (1982) classified the bifurcation diagrams of a cooled tubular reactor by using discretization of the differential equations. The shooting technique was applied by Nielsen and Villadsen (1983, 1985), Witmer et al. (1986), Balakotaiah et al. (1987), and Song et al. (1990) to determine the multiplicity features of distributed reactor models. Subramanian and Balakotaiah (1996) combined an implicit Liapunov-Schmidt reduction with the shooting method to classify the steady state and dynamic features of various diffusion-convection-reaction problems, described by a set of differential equations in one spatial dimension.

Generally, numerical bifurcation techniques require simultaneous solution of the model equations and a set of conditions defining the specific bifurcations. While this procedure can be readily applied to construct the bifurcation maps of stationary states (Uppal et al., 1974, 1976; Vaganov et al., 1978; Balakotaiah and Luss, 1983, 1984, 1988; Farr and Aris, 1986; Subramanian and Balakotaiah, 1996; Balakotaiah et al., 1999) or of periodic states described by a set of ordinary differential equations (Kubícek and Holodniok, 1987), numerical difficulties usually arise in its application to periodic systems described by a set of partial differential equations. Dynamics of periodically operated reactors were extensively analyzed using methods developed by Khinast et al. (1998, 1999, 2000). Highly efficient bifurcation methods based on model reduction (that is, Karhunen-Loeve decomposition) were developed in order to reduce the computational effort (Graham et al., 1995; Graham and Kevrekidis, 1996).

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Detection and tracking of the various singularities and of the possible attractors (steady states, oscillations, quasi-periodic or chaotic dynamics) requires specific knowledge of singularity theory and of numerical methods. For example, the existence of isolated solution branches in cooled CSTR models cannot be detected by continuation methods alone, but the conditions defining the isola variety are required. Other reactors, such as two-phase decanting reactors, show a large number of not-connected solution branches (Harold et al., 1996; Khinast et al., 1998) and it is not guaranteed that all the solution branches are found. Therefore, it would be advantageous to develop simple, not system-specific, methods based on random searches that are able to detect the various attractors in the parameter space.

The objective of this work is to present a novel and efficient method for generating steady-state stability maps of different reactor models. These maps determine the parameters for which stable operating conditions exist, which is useful for the design and operation of chemical reactors. Typically, one is interested only in the stability of a reactor steady state. Since the local stability of a steady state is uniquely determined by its eigenspectrum, the eigenvalues can be used to identify parameter regions, where no intricate dynamics are expected. Additionally, these methods can be used to identify certain simple singularities like Hopf and limit points that bound regions of oscillatory behavior and multiple steady states. Methods based on random searches cannot guarantee the determination of every existing attractor, nor convergence to a particular (complex) steady state. However, the same limitations are shared by all local optimization methods, and can only be rectified by the development of global optimization procedures, which are currently an active field of research.

The proposed methodology is intended to complement traditional bifurcation analysis based on continuation techniques and singularity theory. The advantage of the presented method is that it can readily determine regions of complex behavior, where detailed bifurcation analysis should concentrate. In addition, it rapidly determines operation criteria for industrial processes, which are usually based on the stability of a steady state.

The algorithm is presented in the next section for determining stability maps of general reactor models, whereas in the following section the algorithm is illustrated by applying it to a cooled CSTR. Although the CSTR is a low-order dynamical system, we used this example to demonstrate the applicability of the proposed methodology. Further studies on higher-order systems are currently performed. Finally, the implementation of the method is discussed.

New Stability Analysis Approach

The proposed approach is based on the ideas of systematic sampling of the parameter space (Diwekar and Kalagnanam, 1997) and utilization of optimization techniques (Gill et al., 1986) to determine the system's steady state that satisfy certain stability criteria. In particular, the proposed procedure consists of the following steps:

• **Step 1:** Application of sampling algorithm to generate points within the parameter range of interest.

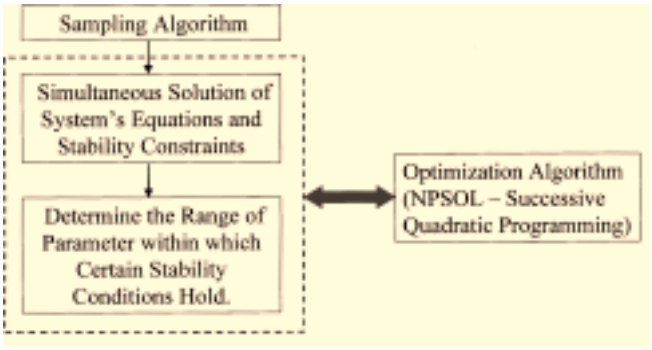

Figure 1. Basic structure of the proposed approach.

• **Step 2:** Simultaneous solution of the system's steady-state equations and stability constraints so as to move from a randomly selected point to a parameter set that corresponds to a specific range on the bifurcation map. Hereby, the density of points located at the boundary between stable and unstable regions is high, thus clearly defining the stability boundaries.

• **Step 3:** Evaluation of the range of parameters within which certain stability conditions are valid.

The proposed procedure is shown in Figure 1. The advantages of the proposed approach are:

• Traditional bifurcation analysis requires first the computation of bifurcation diagrams using continuation techniques and second the determination and analysis of the singular points again with the help of continuation methods. The approach proposed in this article is a single-stage procedure where the system's steady state is determined to satisfy the imposed stability criteria. Thus, it is easier and more straightforward to use.

• The approach is general as to consider any number of operating and design parameters with no increase in the computational requirements.

• Step 2 can be used as a pre-processing step for any stability analysis resulting in an approximation of the bifurcation map.

• Step 3 results in the evaluation of the critical parameter range by the solution of a single optimization problem.

In the next section a cooled CSTR is used to illustrate and further clarify the basic steps and results of the proposed approach.

Stability of a Cooled CSTR

A continuously stirred tank reactor (CSTR) is a reaction vessel with a continuous feed and effluent stream. The dynamic behavior of CSTRs have been used by many researchers (Uppal et al., 1974; 1976; Balakotaiah and Luss, 1983) to test different methods of bifurcation analysis. The dimensionless model equations are given by

$$\frac{dx}{d\tau} = Da\exp\left(\gamma\frac{\theta}{1+\theta}\right)\cdot(1-x) - x \qquad (2)$$

$$Le\frac{d\theta}{d\tau} = -\theta - \Delta(\theta-\theta_c) + DaB\cdot(1-x)\cdot\exp\left(\gamma\frac{\theta}{1+\theta}\right) \qquad (3)$$

with the dimensionless variables

$$\theta = \frac{T - T_f}{T_f}, \quad x = \frac{c_o - c}{c_o}, \quad \tau = \frac{tq}{V} \tag{4}$$

In Eq. 4 q is the volumetric feed and effluent rate, V is the volume of the reaction vessel, T_f is the feed and coolant temperature, and c_o is the feed concentration. The dimensionless parameters are

$$\boldsymbol{p} = \left\{ Da = \frac{k(T_f)V}{q}, \quad \Delta = \frac{\alpha A}{q\,\rho c_p}, \quad Le = \frac{m_R c_{p,R} + \rho c_p V}{\rho c_p V}, \right.$$
$$\left. \gamma = \frac{E_a}{RT_f}, \quad B = \frac{(-\Delta H)c_o}{\rho c_p T_f}, \quad \theta_c = \frac{T_c - T_f}{T_f} \right\} \tag{5}$$

with

$$k(T_f) = k_\infty \cdot \exp\left(\frac{E_a}{RT_f}\right) \tag{6}$$

In Eq. 5, it can be assumed that the Le-number for industrial-sized CSTRs is unity. At steady state, the righthand side of Eqs. 2 and 3 become zero. Therefore

$$\boldsymbol{F}(x,\theta,\boldsymbol{p}) = \begin{Bmatrix} Da\exp\left(\gamma\frac{\theta}{1+\theta}\right)\cdot(1-x) - x \\ Le^{-1}\cdot\left[-\theta - \Delta(\theta - \theta_c) + DaB\cdot(1-x)\cdot\exp\left(\gamma\frac{\theta}{1+\theta}\right)\right] \end{Bmatrix} = \mathbf{0} \tag{7}$$

Stability and bifurcation points can be found by performing a local linear stability analysis around a steady state, that is, for a given steady state, the Jacobian matrix of Eq. 7 and its eigenvalues are determined. If there exists at least one eigenvalue with a real part larger than zero, the steady state is unstable. If all eigenvalues are smaller than zero, a steady state is stable. Typically, stability is lost (or regained) at two critical bifurcation points, that is, at a limit (turning) point or at a Hopf point. In the case of a limit point one real eigenvalues is equal to zero, whereas at a Hopf point a complex conjugate pair of eigenvalues has a zero real part. The situation is illustrated in Figure 2. On one side of the limit point, two

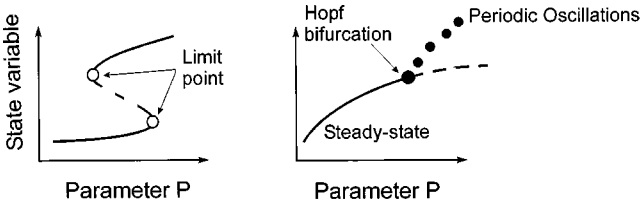

Figure 2. Limit and Hopf point.

——— = Stable steady state; – – – – = unstable steady state; ●●●● = maximum amplitude of oscillatory states.

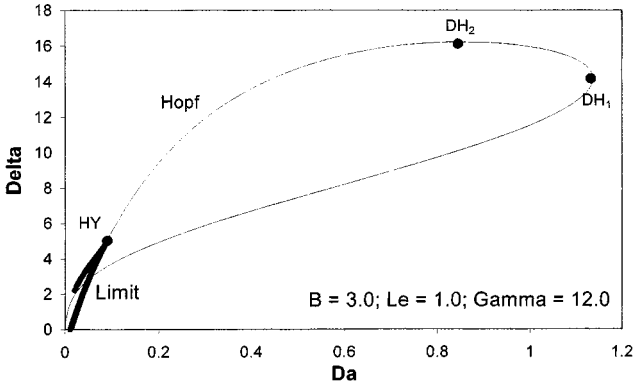

Figure 3. Limit and Hopf points of a cooled CSTR.

Bold line = limit point; thin line = Hopf.

solutions and on the other side no solution exists. On one side of the Hopf point, oscillations exist; on the other side, the steady state is stable. Often the situation is more complex since degenerate or subcritical bifurcations exist, which are not considered here.

Once a limit point or Hopf point is located, it can be tracked with respect to another parameter, to generate a bifurcation map. In Figure 3 a bifurcation map in the plane of the cooling capacity Δ and the Damköhler number Da is shown for constant values of B, Le, and γ. In the region between the two limit points multiplicity exists, that is, there exist three steady states. To the right of the hysteresis point (HY), no multiplicity exists. In the area between the Hopf points oscillatory solutions exist, that is, the temperature and conversion of the reactor will change periodically. To the right of the double-Hopf point DH_1 and above DH_2, no oscillatory solutions exist.

The fine details of the map, like the intersection of Hopf and limit point, are not discussed here, since it is beyond the scope of this article. Note that it is usually avoided to operate within the oscillatory region, because the temperature amplitudes can reach values higher than those of the corresponding steady state. This may lead to thermal runaway or to the ignition of undesired side reactions, which may reduce selectivity and cause safety problems. For the same reason, operation in the multiplicity region is avoided (or at least good temperature control has to be implemented) since a small change in an operation parameter may lead to a sudden large change of the temperature (ignition-extinction behavior).

Clearly, bifurcation analysis is highly useful, but it is time-consuming to first compute bifurcation diagrams using continuation techniques, to find the singular points, and to track the singular points in the parameter space using continuation.

The proposed methodology is employed here (for the same Le, B, and γ as in Figure 2) as an alternative approach in order to evaluate the stability of the reactor system under different operating conditions. We begin our analysis by determining the stable region in the parameter space (Da, Δ). For this purpose, an iterative scheme is applied. First, a point (Da, Δ) is generated randomly, using a pseudo-random generator, within the range of interest. Then, Eq. 7 is solved simultaneously with the stability conditions, that is, all the

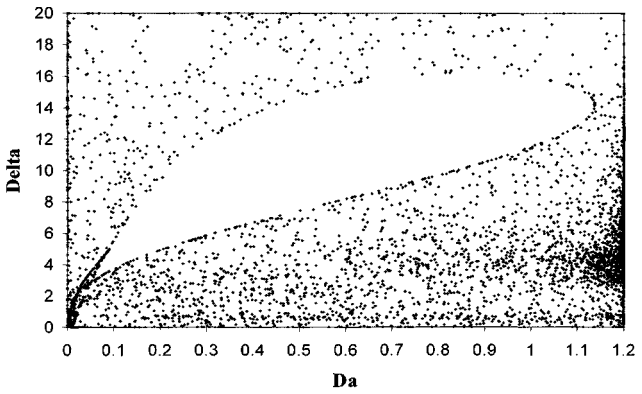

Figure 4. Stable region.

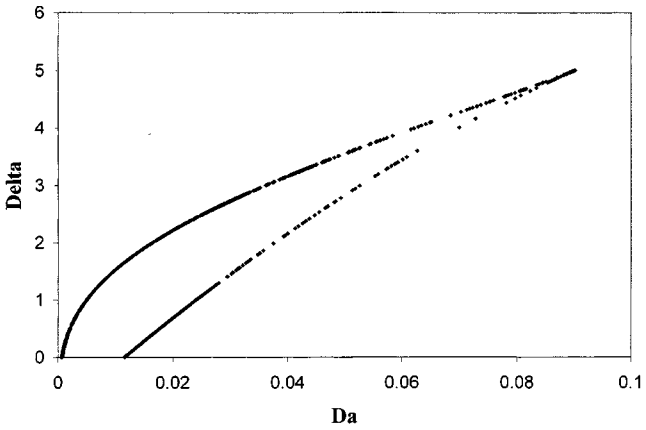

Figure 6. Limit points.

eigenvalues of the Jacobian matrix of Eq. 7 have negative real parts. Thus, the mathematical problem solved in this case is the following

$$\min \quad RHS^2 \quad \text{subject to}$$

$$F(x,\theta,p) = \mathbf{RHS} \tag{8}$$

$$Re\{\lambda_i\} < 0 \tag{9}$$

where λ_i are the eigenvalues of the Jacobian of Eq. 7.

The variables of the above optimization are x, θ, and (Da, Δ). Consequently, at the solution where the objective function is zero, the point (Da, Δ) is determined to satisfy Eq. 7 and the stability constraints. The problem was solved using a nonlinear optimization solver NPSOL (Gill et al., 1986), which is based on a successive quadratic programming algorithm. This algorithm can solve general nonlinear programming problems with nonlinear objective function and a set of constraints on variables. The algorithm proceeds iteratively by: (a) solving a quadratic approximation of the nonlinear problem; (b) using line-search to determine the direction and step length of the next variable updates; and (c) updating the approximation of the Hessian of the Lagrangian function.

The results obtained after 10,000 iterations are shown in Figure 4. It is important to note that Figure 4 is a valid approximation of the stable region in the bifurcation map in Figure 3. Moreover, the boundary between the stable and unstable region is well defined. In this line of thinking the same iterative procedure is used to generate the unstable region. The stability constraints for the results shown in Figure 5 have the following form

$$\max_i \{ Re\{\lambda_i\} \} > 0 \tag{10}$$

In addition to these results the proposed approach is extended to determine the limit and Hopf points. The corresponding stability conditions are

$$\exists i \in I \,|\, \{ Re\{\lambda_i\} = 0 \vee Im\{\lambda_i\} = 0 \} \tag{11}$$

for the limit points and

$$\exists i \in I \,|\, \{ Re\{\lambda_i\} = 0 \vee Im\{\lambda_i\} \neq 0 \} \tag{12}$$

for the Hopf points, where I is the set eigenvalues of the Jacobian of Eq. 7. The results using 10,000 iterations are shown in Figures 6 and 7, respectively. Another important extension of the proposed methodology is the capability to

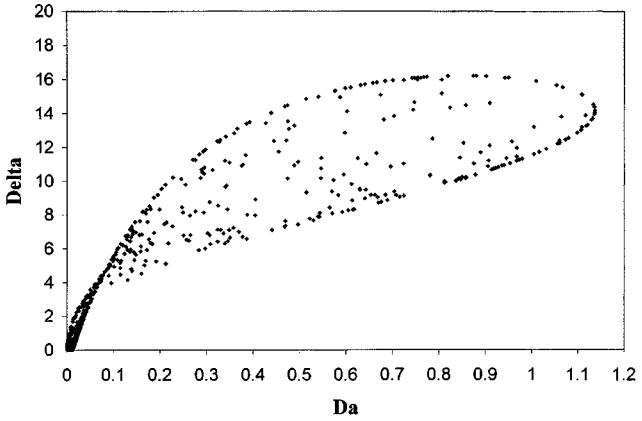

Figure 5. Unstable region.

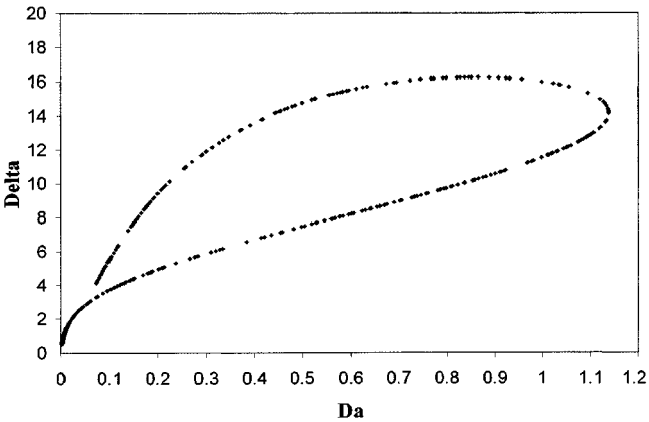

Figure 7. Hopf points.

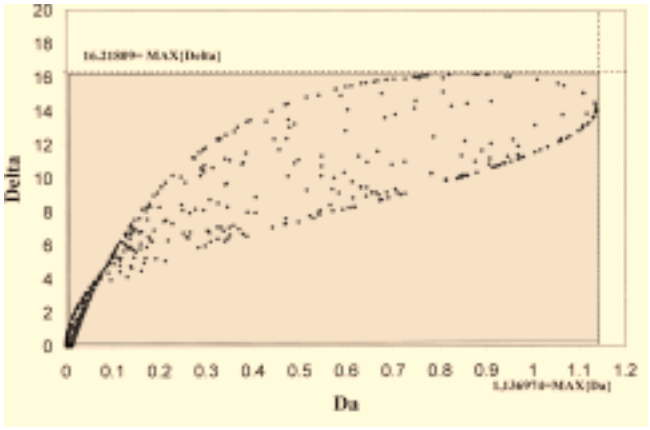

Figure 8. Safe range of operating conditions.

determine the bounds of the parameter space where certain stability conditions hold true as outlined in Step 3. The general mathematical formulation has the following form

$$\min P^l - P^u \text{ subject to } \boldsymbol{F}(x,\theta,\boldsymbol{p}) = \boldsymbol{0}$$
$$\text{and the stability constraints} \quad (13)$$

where l and u denote the lower and upper bound of the parameter of interest $P \in \boldsymbol{p}$. For the cooled CSTR, the maximum levels of Da and Δ are determined subject to conditions of instability. This then determines the safe region of operating conditions outside the shaded area in Figure 8.

Discussion and Summary

The proposed algorithm is intended to provide design engineers with a straightforward tool to examine the stability of different chemical reactor systems. The algorithm randomly samples operating conditions and subsequently checks the corresponding stability. The approach becomes especially powerful since optimization is used to satisfy a desired stability constraint. As a consequence, the boundary between a stable and an unstable region can be determined conclusively. The algorithm is also general, as it can find and track limit and/or Hopf points.

Currently, we are working on improving the efficiency of the proposed approach so as to enable its use for complex reactor systems. The issues we are investigating are the following:

- Extend the current methodology to higher-order dynamical systems.
- Explore different, more efficient sampling techniques such as Hammersley Sequence Sampling (HSS) (Diwekar and Kalagnanam, 1997). This will improve the efficiency of the proposed methodology since it will result in a reduced number of iterations required to generate the map on the parameter space.
- Investigate the utilization of alternative optimization algorithms, especially considering derivative free approaches such as Direct Search methods (Reklaitis et al., 1983).

The presented approach of combining optimization, random search, and bifurcation analysis can be a powerful tool for analyzing the stability of chemical reactors or separation units. Further improvements, that is, the use of global optimization methods, or the combination with traditional continuation methods, may lead to a universal tool for the bifurcation analysis of complex dynamical systems.

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