Stability in Optimal Design: Synthesis of Complex Reactor Networks

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A systematic methodology applicable to the optimal design of stable process systems is presented. It is based on the formulation of a parametric problem that provides bounds on the optimal stable solution and an iterative algorithmic approach that attains convergence of the bounds in a finite number of iterations. The bounds on the optimal stable solution are based on analytical expressions of bounds on the eigenvalues of the Jacobian matrix using the concept of the measure of the matrix. When extended to the synthesis problem of reactor networks, the approach is able to couple the optimization problem with stability issues even in cases where the number of reactors is large and the reaction mechanism is described by a general complex reaction scheme. Furthermore, since at the synthesis level the reactor network represents an exhaustive superposition of the existing structural and operational alternatives, the approach fully exploits these alternatives and coordinates a weighted optimal search that improves the objective and accommodates a stable reactor network. This approach is not restricted to the synthesis of reactor networks and can be applied to the design of total process flowsheets.

Introduction

The general character of the steady-state operation of the continuous stirred tank reactor has been first studied by Liljenroth (1918) and much later by Frank-Kamenetski (1939) and Salnikov (1948) who discussed the problem of periodic phenomena in a reaction system. Bilous and Amundson (1955) first viewed the CSTR as a nonlinear dynamic system, applied Lyapunov's indirect method to study different steady states, developed analytical criteria for the stability, and presented phase portraits for the reaction paths of the system. In the following two decades, a much better understanding of the problem has been achieved through a large number of theoretical and experimental studies focused on the development of: (i) methods pertaining to the dynamical system in terms of its possible phase portraits and bifurcation diagrams; (ii) systematic methods for calculating the maximum number of solutions and the different types of steady-state bifurcation diagrams; and (iii) uniqueness and steady-state multiplicity criteria expressed in terms of the system parameters.

In the first class of achievements belong the phase planes by Uppal et al. (1974, 1976), the augmented portrait galleries presented by Vaganov et al. (1978), Williams and Calo (1981), Kwong and Tsotsis (1983) and Pismen (1984), as well as the deterministic chaos observed and studied in a number of cases concerning reaction processes. In the second class of developments belong the early works by Aris and Amundson (1958a,b,c) and the methods of singularity theory for systems with a distinguished parameter developed by Golubitsky and Schaeffer (1979). These methods were applied by Golubitsky and Keyfitz to the single-reaction CSTR (1980) and by Balakotaiah and Luss (1981, 1982a,b,c, 1983, 1984) to a more general spectrum of reaction schemes.

The multiplicity problem has been addressed for a number of cases that range from the single irreversible reaction to mechanisms described by consecutive and parallel reaction schemes. For the case of two consecutive reactions the maximum multiplicity has been found to be seven (Chicone and Retzloff, 1981). As the number of the consecutive reactions increases to n, the maximum number of solutions increases to as high as $2^{n+1}-1$ (Chicone and Retzloff, 1981). For two parallel reactions the multiplicity around the highest order sin-

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gularity is five (Balakotaiah and Luss: 1982a, 1983) and in the general case of n parallel reactions with the equal and sufficiently large activation energies, there are $(n!)$ singular points with maximum multiplicity $2n+1$. These results, all in reference to the single CSTR, give an idea of the complications behind the general problem associated with a complex reaction mechanism.

A systematic work on the multiplicity and stability problem of two nonisothermal CSTRs can be found in an exceptional article by Kubicek et al. (1979) who studied the effect of the recirculation ratio on the stability, and they concluded that the multiplicity of the system is decreased as the recycle increases. Dangelmayr and Stewart (1982) viewed the N-CSTR cascade as a sequential bifurcation problem while Svoronos et al. (1982) extended the work by Uppal et al. (1974, 1976) for the case of two identical CSTRs in series and provided a test for the direction of bifurcations of limit cycles. The derivation of conditions for uniqueness and multiplicity has been studied for a number of single and multiple-step reactions. In terms of general criteria, Feinberg and Horn (1974, 1977) and Feinberg (1987), whose work has its roots in the ideas of Horn (1972, 1973) and Horn and Jackson (1972), developed an analysis for the stability of isothermal reactor networks for which a number of properties (deficiency, reversibility, weak reversibility, and so on) is defined and two principal theorems are proved for networks with deficiency zero and one. Although networks of high deficiency arise often in practice, Feinberg's work has been the first systematic effort to have addressed the stability of complex reactor networks.

Westerterp and Jansma (1985) studied the safe design and operation of tank reactors for multiple reactions and developed uniqueness and multiplicity criteria using Van Heerden's analysis (1953) based upon the construction of curves for the heat withdrawal and production rate. The authors found difficult to handle the design problem with the available criteria in the literature and developed a methodology based upon a plotting of the design and operating constraints in a diagram of dimensionless groups. These ideas were further extended for the safe design of cooled tubular reactors for exothermic reactions (Westerink and Westerterp, 1990a), the safe design and operation of fluidized-bed reactors (Westerink and Westerterp, 1990b) and the stable design and operation of catalytic fluidized-bed reactors (Westerink and Westerterp, 1990c).

This article presents a systematic approach for the design of stable reactor networks. The problem is addressed at the synthesis level where the design parameters have not yet been specified and the focus is on constructing a stable reactor configuration that optimizes a given performance criterion. The optimization objectives require the use of explicit criteria for stability. Although for simple mechanisms such criteria may be available, it is for the synthesis of processes described by complex reaction mechanisms the use of reactor networks is justified. Furthermore, instead of a single unit, the reactor network consists of many reactors and, since the optimal configuration is a special case of a general structure inclusive of all possible interconnections among the units and featuring options for side streams and recycles, the analysis should be capable of handling systems comprised of a large number of parameters and variables.

The motivation and synthesis objectives addressed in this article are presented, as well as a review of the concepts the proposed approach is based on. These concepts include the basic definitions of the matrix measures and their properties, as well as theorems defining their relation to the dynamics of a particular system. Then, the general problem of optimizing a nonlinear system over its stable equilibrium points is addressed. A systematic procedure is further developed which leads to the optimal stable solution of the problem is of general applicability, and accommodates for large-scale implementations. The approach is applied to the optimal synthesis of reactor networks that feature complex reaction mechanisms and/or networks of reactors which are highly interconnected and account for a complete representation of the synthesis alternatives.

Motivation and Synthesis Objectives

At the synthesis level, an isothermal or a nonisothermal reactor network superstructure represents an exhaustive superposition of the available alternatives of the reactor system and embeds design scenarios one may take advantage of in order to improve the performance of the reaction process. The solution of this problem results in a reactor configuration which although optimal does not, in general, represent a stable operating system. In the case of inexpensive control action and perfect controllability, such an unstable solution may still be the desired alternative for the reaction mechanism in question. There are cases, however, for which either the controllability over the reaction process is limited or one is willing to know about the tradeoffs between the unstable operation and the required control action. Meeting stability concerns for the optimal solutions obtained by the reactor network synthesis approaches have been the motivation behind the analysis presented in this work.

The effort in stabilizing a reactor system is often attained by manipulating the operating parameters of the process (that is, inlet temperature, utility consumption, overall conversion, and so on) at an *a posteriori* stage. It is possible, however, that structural parameters may be of equal importance and as such one may consider the potential rearrangement of units, the reallocation or redistribution of the feed, the reallocation or conversion of utilities, as well as the consideration of bypasses, recycles, or other interconnecting streams.

Thus, it seems advantageous to develop a methodology that looks into the stability problem within a superstructure scheme. In such an approach, should the criteria for the performance also include stability considerations, the different features of the superstructure are to be fully exploited so as to maintain the desired dynamic characteristics for the system. Therefore, the analysis effort should not focus on stabilizing a subsystem of the reference structure; such an effort would only consist in a local search around an unstable optimal solution and, if successful, would end up at a suboptimal solution. In contrast to a local search, the desired methodology has to search for stable systems in the entire vector space and meet the optimality conditions in the final solution.

The mathematical formulations associated with reactor network superstructures consider a large number of state variables and a general class of nonlinearities depending on the expressions of the kinetics, the isothermal or nonisothermal operation of the process and the mixing alternatives of the superstructures. In order to accommodate the additional considerations,

the approach should be able to handle the size and the structure of these formulations and, in reference to the general case, not to restrict itself to specific types of reaction mechanisms or reaction rates. Therefore, outlining the principal objectives, the stability problem should be:

(i) Addressed *at the synthesis level* along with the superstructure alternatives
(ii) Coupled with the optimization problem via *explicit* criteria
(iii) Embedded in the *nonlinear* and generally *large* formulations that handle complex reaction networks
(iv) Solved with a *systematic* and rigorous algorithmic procedure.

On asymptotically stable equilibrium points, Lyapunov's indirect method enables one to draw conclusions about a nonlinear system by studying the eigenvalues of the Jacobian matrix of the linearized system. At the synthesis level at which the configuration of a system of reactors is unknown, however, the Jacobian matrix is not numerically available but only as a general function of the unknown equilibrium point. As a result, mathematical expressions for the eigenvalues can only be obtained for very small and up to 4 by 4 systems. Furthermore, even in these cases, the expressions are highly nonconvex and quite complex to be accommodated in the optimization problem. Instead of the eigenvalues, one could alternatively focus on the derivation and use of analytical expressions for the bounds of the eigenvalues. As it is shown later, in this case the expressions are found to be simple, convex and, what is most important, able to handle arbitrarily large systems. Further discussion on the subject gives reference to the measure of a matrix (Dahlquist, 1959; Coppel, 1965) which is presented in the following section.

Review of Basic Concepts

Definition 1

Let $\|\cdot\|$ be a norm function and A be a matrix in $\Re^{n\times n}$. The mapping $\Re^{n\times n}\rightarrow\Re$:

$$\|A\|_i = \sup_{x\neq 0}\frac{\|Ax\|}{\|x\|} = \sup_{\|x\|=1}\|Ax\| = \sup_{\|x\|\leq 1}\|Ax\| \tag{1}$$

is called the induced norm of A.

The induced matrix norms corresponding to the vector norms $\|\cdot\|_\infty$, $\|\cdot\|_1$ and $\|\cdot\|_2$ are given in Table 1.

Table 1. Induced Norms on $\Re^{n\times n}$

Norm on $\Re^n$	Induced Norm
$\|\cdot\|_1 = \sum_{i=1}^{n}\|x_i\|$	$\|A\|_{i1} = \max_j \sum_i \|\alpha_{ij}\|$
$\|\cdot\|_2 = \left(\sum_{i=1}^{n}\|x_i\|^2\right)^{1/2}$	$\|A\|_{i2} = \{\lambda_{\max}(A^*A)\}^{1/2}$
$\|\cdot\|_\infty = \max_i \|x_i\|$	$\|A\|_{i\infty} \max_i \sum_j \|\alpha_{ij}\|$

Definition 2

Let $\|\cdot\|_i$ be an induced matrix norm on $\Re^{n\times n}$. The matrix measure or the logarithmic derivative of a matrix A of $\Re^{n\times n}$ is the mapping μ_i: $\Re^{n\times n}\rightarrow\Re$:

$$\mu_i(A) = \lim_{\epsilon\rightarrow 0^+}\frac{\|I+\epsilon A\|_i - 1}{\epsilon} \tag{2}$$

As by the above definition, $\mu_i(A)$ is the directional derivative of the norm in the direction of the matrix A. A detailed discussion about the matrix measure, its full set of properties, as well as the analytical results based upon the various classes of norms can be found in Desoer and Haneda (1972), Desoer and Vidyasagar (1975), and Kokossis (1992). This section provides an introduction to the subject and outlines the properties which are of importance for the synthesis objectives of this work.

Property 1. The matrix measure $\mu_i(A)$ exists $\forall A$ in $\Re^{n\times n}$ and for every induced norm $\|\cdot\|_i$.

Property 2. The matrix measure function is sign-sensitive and bounded by the positive (upper bound) and negative (lower bound) induced norm functions.

Property 3. If μ_i is a measure function on $\Re^{n\times n}$, then $\forall\alpha\in[0, +\infty]$, μ_i is a multiplicative function:

$$\mu_i(\alpha A) = \alpha\mu_i(A), \quad A\in\Re^{n\times n} \tag{3}$$

μ_i is a convex function, namely:

$$\mu_i\{\alpha A + (1-\alpha)B\} \leq \alpha\mu_i(A) + (1-\alpha)\mu_i(B) \tag{4}$$

for every A and B in $\Re^{n\times n}$ and $\forall\alpha\in[0, 1]$.

Theorem 1. Let $\|\cdot\|$ be a norm in $\Re^n$ and $\|\cdot\|_i$, μ_i denote the corresponding induced norm and matrix measure on $\Re^{n\times n}$. Also assume the linear system:

$$\dot{x}(t) = A(t)x(t) \tag{5}$$

where $x(t)\in\Re^n$ and $A(t)$ is piecewise continuous. Then:

$$\|x(t_0)\|\exp\left\{\int_{t_0}^{t} -\mu_i(-A(\tau))d\tau\right\} \leq \|x(t)\| \leq \|x(t_0)\|\exp\left\{\int_{t_0}^{t}\mu_i(A(\tau))d\tau\right\} \tag{6}$$

for every $t\geq t_0\geq 0$.

Theorem 2. For every eigenvalue λ_k, $k=1, \ldots, n$ of the matrix $A\in\Re^{n\times n}$ and for every induced norm $\|\cdot\|_i$:

$$-\mu_i(-A) \leq Re(\lambda_k) \leq \mu_i(A) \tag{7}$$

From theorem 1, it follows that, with respect to the solution of a dynamic system, bounding expressions can be derived in terms of $\mu_i(A)$. Furthermore, from both theorems it follows that a sufficient condition for asymptotic stability is that the measure matrix $\mu_i(A(t))$ is a negative function. For autonomous systems, theorem 2 provides an explicit criterion for the

Table 2. Matrix Measures on $\Re^{n\times n}$

Norm on $\Re^n$	Matrix Measure
$\|\cdot\|_1=\sum_{i=1}^{n}\|x_i\|$	$\mu_1(A)=\max_j\left\{a_{jj}+\sum_i\|a_{ij}\|\right\}$
$\|\cdot\|_2=\left(\sum_{i=1}^{n}\|x_i\|^2\right)^{1/2}$	$\mu_2(A)=\lambda_{\max}[A^*+A]/2$
$\|\cdot\|_\infty=\max_i\|x_i\|$	$\mu_\infty(A)=\max_i\left\{a_{ii}+\sum_j\|a_{ij}\|\right\}$

nonnegative of A whenever analytical expressions are available for $\mu_i(A)$. However, based upon an arbitrary norm, such expressions are not generally possible. For the norms $\|\cdot\|_1$, $\|\cdot\|_2$, and $\|\cdot\|_\infty$, the matrix measures take on the explicit mathematical forms given on Table 2. In conjunction with these forms, the applicability of theorem 2 is further illustrated with an example.

Illustration

Let the matrix:

$$A=\begin{bmatrix}6 & -3\\ 3 & 2\end{bmatrix}$$

The eigenvalues of A are given by:

$$\lambda_{1,2}=4\pm i\sqrt{5}$$

while the matrix measures of A are given by:

$$\mu_1(-A)=1 \quad \mu_1(A)=9$$

$$\mu_2(-A)=2 \quad \mu_2(A)=6$$

$$\mu_\infty(-A)=1 \quad \mu_\infty(A)=9$$

Since $Re(\lambda_1)=Re(\lambda_2)=4$, theorem 2 can be verified through the validity of the following inequalities:

$$1=\mu_1(-A)\le Re(\lambda_{1,2})\le\mu_1(A)=9$$

$$2=\mu_2(-A)\le Re(\lambda_{1,2})\le\mu_2(A)=6$$

$$1=\mu_\infty(-A)\le Re(\lambda_{1,2})\le\mu_\infty(A)=9$$

In the above illustration, the matrix A has constant elements and its eigenvalues can be calculated analytically. For a matrix whose elements are not constant, the matrix measures will still provide upper and lower bounds for the real parts of the eigenvalues even if the evaluation of the eigenvalues is not possible. This is the case of dynamical systems whose steady-state performance is to be optimized and the matrix A consists of elements that represent unspecified design parameters. For these systems, Lyapunov's indirect criteria for asymptotic stability cannot be implemented and the use of matrix measures represents an attractive alternative: (i) the measures have desired convexity properties (part (ii) of Property 3), and (ii) mathematical expressions for the measures based upon the norms $\|\cdot\|_1$ and $\|\cdot\|_\infty$ (see Table 2) are particularly suitable to optimization purposes because the maximization terms of these expressions can be always relaxed into a set of inequality constraints. Although both can be used for bounding the eigenvalues of A, there is no way of predicting which one performs better. In general they both can be very conservative and this issue gives rise to the matrix measure relaxation approach which is presented in the following section.

Optimal Design of Stable Systems

Problem definition

Let $x\in\Re^n$ be a vector of variables and $p\in\Re^m$ a vector of parameters of the nonlinear dynamical system (M):

$$\dot{x}(t)=g(x,p)$$
$$x\in X$$
$$p\in Z \tag{8}$$

where $g(x,p)$ is a continuously differentiable function in terms of x. Let also the Jacobian:

$$G(x,p)=\left[\frac{\partial g(x,p)}{\partial x}\right]_x \tag{9}$$

be a well defined function $\forall(x,p)\in X\times Z$. The steady-state solution of (M) is given by:

$$F=\{y\in X\times Z:\quad g(y)=0\} \tag{10}$$

and the set of stable equilibrium points by:

$$S=\{y\in F:\quad \lambda[G(y)]<0\} \tag{11}$$

For a given function $f(x,p)$ on $\Re^{n\times m}$—a minimizing direction can be assumed without any loss of generality—the objective is the solution of the problem (P_1):

$$z=\min_{(x,p)\in S} f(x,p)=f(x^*,p^*) \tag{12}$$

Parametric problem

Let $G(x,p)$ denote the Jacobian matrix with elements $g_{i,k}$, $i,k=1,\ldots,n$. Based upon the $\|\cdot\|_\infty$ norm, the matrix measure μ of G is given by:

$$\mu[G(x,p)]=\max_{1\le k\le n}\omega_k \tag{13}$$

where

$$\omega_k=g_{k,k}+\sum_{\substack{i=1\\ j\ne k}}^{n}|g_{i,k}| \tag{14}$$

If $b \in [b^{lo}, b^{up}]$ stands for the n-dimensional vector $(b_1, b_2, \ldots, b_n)^T$, the parametric problem $P(b)$ is defined as:

$$z(b) = \min f(x, p)$$

$$g(x, p) = 0$$

$$\omega_k \le b_k \quad k = 1, \ldots, n$$

$$x \in X$$

$$p \in Z \tag{15}$$

The following theorem is proved in Appendix A.

Theorem 3. Let F be a compact set along with the function $z: \Re^n \to \Re: b \to z(b)$, where $z(b)$ is the solution of the parametric problem $P(b)$. Then:

(a) z is a nonincreasing function; and

(b) There exists a $z_\infty \in \Re$ such that: (i) $z_\infty = \lim_{b \to \infty} z(b) = f(x_\infty, p_\infty)$; and (ii) $z_\infty = z^{lo}$ where z^{lo} is the solution of the optimization problem (P_2):

$$z^{lo} = z(b^{up}) = \min_{y \in F} f(y) \tag{16}$$

If b^{lo} represents an n-dimensional vector for which $P(b)$ is feasible, then it represents an upper bound on $z(b)$, that is, $z^{up} = z(b^{lo})$ and for $b^{lo} = 0$ we have:

$$z(b^{lo}) \in S \tag{17}$$

Then since $z(b)$ is the solution of (P_1), it holds that:

$$z^{lo} = z(b^{up}) \le z(b) \le z(b^{lo}) = z^{up} \tag{18}$$

As stated in the above inequality, the solution of (P_1), z, is bounded by two of the solutions of the parametric problem: the upper bound corresponds to a stable equilibrium point while the lower bound corresponds to an unstable solution. From theorem 3 it holds that $\exists b^* \in [b^{lo}, b^{up}]$ such that $z = z(b^*)$. If the components of the n-dimensional function h: $\Re^n \to \Re$: $b \to \max_\lambda \mathrm{Re}\{\lambda[G(x_b, p_b)]\}$ are continuous and unimodal, the search of b^* can be directed by any conventional optimization approach. In the more general case the problem has to be viewed as an optimization of a multivariate Lipschitz function. For this latter class of problems, systematic algorithmic procedures have been proposed by, among others, Evtushenko (1971), Pijavskii (1967), Strongin (1973), and Timonov (1977), as well as approaches based upon decomposition (Floudas and Visweswaran, 1990, 1993; Visweswaran and Floudas, 1990, 1992). As to the absolute values introduced in the formulation of the parametric problem, they can generally be handled by assigning binary variables to the sign of their argument and reformulating the parametric problem as a Mixed Integer Nonlinear Programming Problem (MINLP). Alternative ways which avoid the use of integer variables are discussed in the section on remarks on the solution algorithm.

Algorithmic procedure

The algorithmic procedure suggests an iterative scheme that solves a parametric problem at each iteration, updates b^{lo} and b^{up}, updates the lower and upper bounds for z and checks for convergence. The algorithm assumes the existence of a stable equilibrium point that sets the value of the parametric vector b^{lo}; the vector b^{up} is obtained by the solution of the steady-state optimization problem (P2). For certain classes of problems, as in the case of reactor networks, the existence of a stable equilibrium point cannot only be guaranteed but, furthermore, its search can be systematically incorporated in the solution procedure. The steps of the solution algorithm are next presented as follows:

Step 1. Formulate and solve the steady-state problem (P_2) and let its solution be $z^{lo} = z_\infty$ and (x_∞, p_∞). If (P_2) is feasible, then,

(a) Calculate the eigenvalues $\lambda[G(x_\infty, p_\infty)]$.
(b) If $\lambda[G(x_\infty, p_\infty)] < 0$ then terminate; $z = z_\infty$.
Step 2.
(a) Set $b^{up} = \mu[G(x_\infty, p_\infty)] \cdot I$.
(b) Set $z^{lo} = z_\infty = z(b^{up})$.
(c) Select b^{lo}.
(d) Formulate $P(b)$.
(e) Solve $P(b^{lo})$ for $z(b^{lo})$ and (x, p).
(f) Set $z^{up} = z(b^{lo})$.

Step 3. Check for convergence criteria:
If $|z^{up} - z^{lo}| \le \epsilon$ terminate; $z = z^{lo}$.
Step 4. Update b, $b = b^k$, and solve $P(b^k)$ for z_b^k and (x_k, p_k). Calculate the eigenvalues $\lambda[G(x_k, p_k)]$.
If $\mathrm{Re}(\lambda[G(x_k, p_k)]) < 0$ then, Update: $z^{up} = z(b_k)$, $b^{lo} = b^k$; go to Step 4.
Else update $z^{lo} = z(b_k)$, $b^{up} = b^k$; go to Step 3.

Since it is based upon the successive relaxation of the bounds imposed on the components of ω, the procedure is identified as a matrix measure relaxation approach. The flow diagram of the algorithmic procedure is given in Figure 1.

Illustration

Consider the optimization problem (P):

$$z = \min x_2^2$$

associated with the dynamical system:

$$\dot{x}_1 = x_1^2 + x_2^2 - 1$$

$$\dot{x}_2 = x_1^2 + x_2 - 4p$$

$$0 \le p \le 1$$

$$x_1 \le 0$$

$$-x_2 \le 0$$

In problem P, the vector of variables x is given by x_1 and x_2 and the vector of parameters by p. The optimal steady state is the solution of the problem (P_2):

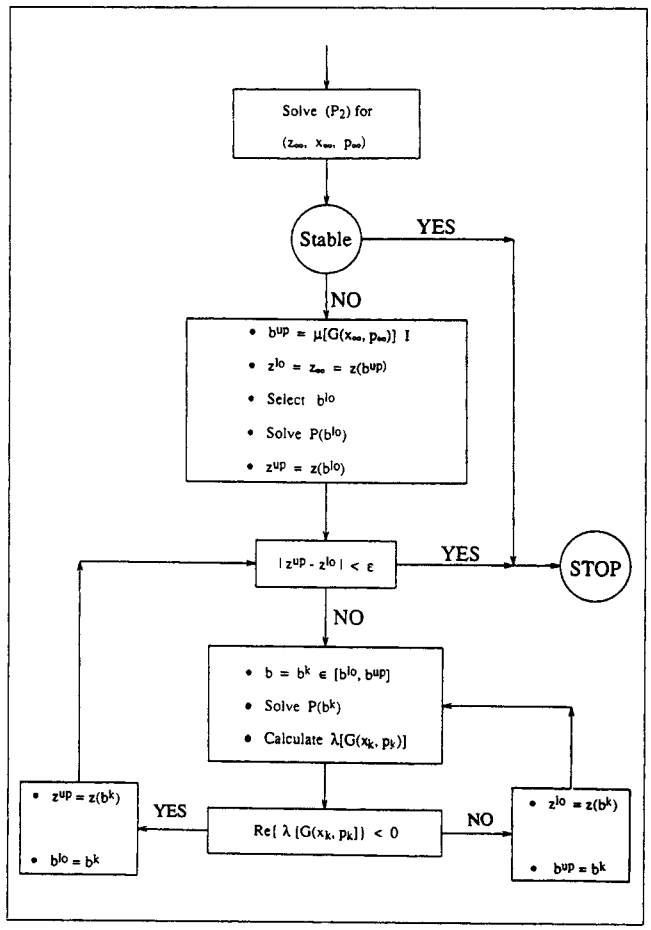

Figure 1. Matrix measure relaxation algorithm.

$$z = \min x_2^2$$

$$s.t \quad x_1^2 + x_2^2 - 1 = 0$$

$$x_1^2 + x_2 - 4p = 0$$

$$0 \le p \le 1$$

$$x_1 \le 0$$

$$x_2 \ge 0$$

and it is given by:

$$z^{\infty} = 0, \quad (x_{\infty}, p_{\infty}) = (-1, 0, 1/4)$$

The Jacobian of the system is:

$$G = \begin{bmatrix} 2x_1 & 2x_2 \\ 2x_1 & 1 \end{bmatrix}$$

and evaluated at (x_{∞}, p_{∞}) yields:

$$G = \begin{bmatrix} -2 & 0 \\ -2 & 1 \end{bmatrix}$$

The eigenvalues of the above matrix are $\lambda_1(G) = -2$ and $\lambda_2(G) = 1$ and since $\lambda_2 \ge 0$, the solution of (P_2) is unstable. The matrix measure of G is:

$$\mu_{\infty}[G(x_{\infty}, p_{\infty})] = \max\{-2, 3\} = 3$$

Set $b^{up} = (3, 3)^T$, $z^{lo} = z(b^{up}) = 0$.

The parametric problem $P(b)$ takes the form:

$$z = \min x_2^2$$

$$s.t \quad x_1^2 + x_2^2 - 1 = 0$$

$$x_1^2 + x_2 - 4p = 0$$

$$2x_1 + 2x_2 - b_1 \le 0$$

$$-2x_1 + 1 - b_2 \le 0$$

$$0 \le p \le 1$$

$$x_1 \le 0$$

$$x_2 \ge 0$$

Iteration 1. By setting the initial parametric vector $b^{lo} = (1.5, 2.0)^T$, the solution of $P(b^1)$ for $b^1 = b^{lo}$ yields:

$$z^1 = 0.75, \quad (x^1, p^1) = (-0.5, 0.866, 0.279)$$

Thus:

$$z^{up} = z^1 = 0.75, \quad z^{lo} = 0.00$$

while in terms of the bounds of the parameter b:

$$b^{lo} = (1.5, 2.0)^T, \quad b^{up} = (3.0, 3.0)^T$$

Iteration 2. Based upon the updated values for b^{up} and b^{lo}, $b^2 = 1/2(b^{lo} + b^{up}) = (2.25, 2.50)^T$ and the solution of $P(b^2)$ is:

$$z^2 = 0.438, \quad (x^2, p^2) = (-0.75, 0.661, 0.306)$$

The eigenvalues of G have negative real parts and the solution is stable. Thus:

$$z^{up} = z^1 = 0.438, \quad z^{lo} = 0.00$$

and

$$b^{lo} = (2.25, 2.50)^T, \quad b^{up} = (3.0, 3.0)^T$$

The iterations further proceed up to the point where:

$$|z^{up} - z^{lo}| \le \epsilon$$

For $\epsilon = 10^{-2}$, the algorithm converges in 6 more iterations:

Iteration	z^{lo}	z^{up}	$(b^{lo})^T$	$(b^{up})^T$	Status of (x^k, p^k)
3	0.23	0.44	(2.25, 2.50)	(3.00, 3.00)	unstable
4	0.23	0.34	(2.25, 2.50)	(2.63, 2.75)	stable
5	0.23	0.29	(2.44, 2.63)	(2.63, 2.75)	stable
6	0.23	0.26	(2.53, 2.67)	(2.63, 2.75)	stable
7	0.25	0.26	(2.58, 2.72)	(2.63, 2.75)	stable
8	0.25	0.25	(2.58, 2.72)	(2.60, 2.74)	unstable

The optimal steady-state solution and optimal vector are therefore given by:

$$z^{opt} = 0.25, \quad (x^{opt}, p^{opt}) = (-0.866, 0.50, 3.125)$$

Optimal Synthesis of Stable Reactor Networks

Linearized single CSTR

The design equations of a CSTR that processes a reaction system of rp reactions and a total of n components are given by:

$$c_p V \frac{dT}{dt} = qc_p(T_o - T) + V \sum_{rp} \Delta H_{rp} R_{rp} - UA(T - T_w) \quad (19)$$

$$V \frac{dc_i}{dt} = q(c_i^o - c_i) + V \sum_{rp} \nu_{rp,i} R_{rp} \quad i = 1, 2, \ldots, n \quad (20)$$

where T_o and c_i^o are the feed temperature and concentration, T_w the coolant or heating fluid temperature and ΔH_{rp} is the molar heats of reaction. The above set of O.D.E.s for the single CSTR is nonlinear only by virtue of the reaction rate term:

$$R_{rp} = R_{rp}(c_1, c_2, \ldots, c_n, T) = R_{rp}(\bar{c}, T) \quad (21)$$

Linearization of R_{rp} around the steady state $R_{rp}^{s.s.} = R_{rp}(\bar{c}_s, T_s)$ yields:

$$R_{rp} = R_{rp}^{s.s.} + \left(\frac{\vartheta R_{rp}}{\vartheta T}\right)_{\bar{c}_s, T_s} (T - T_s) + \sum_{i=1}^{n} \left(\frac{\vartheta R_{rp}}{\vartheta c_i}\right)_{\bar{c}_s, T_s} (c_i - c_{i,s}) \quad (22)$$

Let the dimensionless temperature $\theta = T \cdot c_p / \Delta H_1$ be introduced and the steady state be made the origin of the phase plane by using the deviation variables:

$$x_o = \theta - \theta_s \quad (23)$$

$$x_i = c - c_{i,s} \quad (24)$$

$$r_{rp} = R_{rp} - R_{rp}^{s.s.} \quad (25)$$

The design equations for the CSTR rearrange to:

$$\dot{x}_o(t) = x_o \cdot \left\{ -q/V - u + \sum_{rp} \beta_{rp} \cdot \left(\frac{\vartheta r_{rp}}{\vartheta x_o}\right) \right\} + \sum_{i=1}^{n} \sum_{rp} \beta_{rp} \cdot \left(\frac{\vartheta r_{rp}}{\vartheta x_i}\right) x_i \quad (26)$$

$$\dot{x}_i(t) = \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_o}\right) x_o + \left\{ -q/V + \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_i}\right) \right\} x_i + \sum_{\substack{j=1 \\ j \neq i}}^{n} \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_j}\right) x_j \quad i = 1, 2, \ldots, n \quad (27)$$

where $\beta_{rp} = \Delta H_{rp} / \Delta H_1$, $u = UA/Vc_p$ and

$$\left(\frac{\vartheta r_{rp}}{\vartheta x_o}\right) = \left(\frac{\vartheta r_{rp}}{\vartheta \theta}\right)_{\bar{c}_s, \theta_s} \quad (28)$$

$$\left(\frac{\vartheta r_{rp}}{\vartheta x_i}\right) = \left(\frac{\vartheta r_{rp}}{\vartheta c_i}\right)_{\bar{c}_s, \theta_s} \quad (29)$$

Matrix measures for the linearized network of N CSTRs

Let us consider the network of N CSTRs interconnected to each other in all possible ways. Let also $m_{l,k}$ denote the volumetric flow rates of the interconnecting stream from reactor l to reactor k, and f_k denote the part of the fresh feed stream that is directed to reactor k. The inlet temperature, θ_k^o, as well as the inlet compositions $c_{i,k}^o$ of the kth CSTR are given by:

$$\theta_k^o = \sum_{\substack{l=1 \\ l \neq k}}^{N} (m_{l,k}/q_k)\theta_k + (f_k/q_k)\theta_f^o \quad (30)$$

$$c_{i,k}^o = \sum_{\substack{l=1 \\ l \neq k}}^{N} (m_{l,k}/q_k) c_{i,l} + (f_k/q_k) c_i^o \quad i = 1, 2, \ldots, n \quad (31)$$

where θ_f^o and c_i^o are the feed stream temperature and composition, q_k the inlet volumetric flow rate and $c_{i,k}^o$ the composition of the ith reactant out of reactor l. In terms of the deviation variables introduced before, the linearized design equations for the reactor network are given by:

$$\dot{x}_{o,k}(t) = x_{o,k} \cdot \left\{ -q_k/V_k - u_k + \sum_{rp} \beta_{rp} \cdot \left(\frac{\vartheta r_{rp}}{\vartheta x_o}\right)_{ss,k} \right\} + \sum_{\substack{l=1 \\ l \neq k}}^{N} \frac{m_{l,k}}{V_k} x_{o,l} + \sum_{i=1}^{n} \sum_{rp} \beta_{rp} \cdot \left(\frac{\vartheta r_{rp}}{\vartheta x_i}\right)_{ss,k} x_{i,k} \quad (32)$$

$$\dot{x}_{i,k}(t) = \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_o}\right)_{ss,k} x_{o,k} + \sum_{\substack{l=1 \\ l \neq k}}^{N} \frac{m_{l,k}}{V_k} x_{i,l} + \left\{ -q_k/V_k + \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_i}\right)_{ss,k} \right\} x_{i,k} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \sum_{rp} \nu_{rp,i} \left(\frac{\vartheta r_{rp}}{\vartheta x_j}\right)_{ss,k} x_{j,k} \quad (33)$$

where $x_{o,k}$ and $x_{i,k}$ denote the deviation variables x_o and x_i at the kth reactor. If the matrix of the stoichiometric coefficients is of rank r and the reactor network consists of N CSTRs, the

linearization of the system results to a $(r+1)N\times(r+1)N$ matrix. Based upon the $\|\cdot\|_\infty$ norm, the matrix measure of the linearized network is given by:

$$\mu_\infty(A)=\max_{\substack{1\le m\le r\\ 1\le k\le N}}\omega_{m,k} \tag{34}$$

with

$$\omega_{1,k}=-q_k/V_k-u_k+\sum_{rp}\beta_{rp}\cdot\left(\frac{\partial r_{rp}}{\partial x_o}\right)_{ss,k}+\sum_{\substack{l=1\\ l\neq k}}^{N}\frac{m_{l,k}}{V_k}+\left|\sum_{i=1}^{r}\sum_{rp}\beta_{rp}\cdot\left(\frac{\partial r_{rp}}{\partial x_i}\right)_{ss,k}\right| \tag{35}$$

$$\omega_{m+1,k}=\left\{-q_k/V_k+\sum_{rp}\nu_{rp,m}\left(\frac{\partial r_{rp}}{\partial x_i}\right)_{ss,k}\right\}+\sum_{\substack{l=1\\ l\neq k}}^{N}\frac{m_{l,k}}{V_k}+\left|\sum_{rp}\nu_{rp,m}\left(\frac{\partial r_{rp}}{\partial x_o}\right)_{ss,k}\right|+\sum_{\substack{j=1\\ j\neq m}}^{r}\left|\sum_{rp}\nu_{rp,m}\left(\frac{\partial r_{rp}}{\partial x_j}\right)_{ss,k}\right| \tag{36}$$

Notice that for $r\ge 2$, explicit expressions for the eigenvalues of the linearized system are not possible unless $N=1$ (that is, single CSTR). Through the matrix measures explicit expressions for the upper and lower bound of the eigenvalues can be obtained for any number of reactors or independent reaction components. Furthermore, in case one is interested in augmenting the design equations so that to include sufficient criteria for stability (that is, $\lambda(A)\le 0$), the criteria should take the form:

$$\omega_{m,k}\le 0 \quad 1\le k\le N, \quad 1\le m\le r+1 \tag{37}$$

Due to the nature of the matrix measure, such criteria may unnecessarily restrict or even eliminate the feasible region. The possibility for such an unfortunate outcome, suggests that the criteria be used in a relaxed form and in combination with the systematic procedure suggested by the matrix measure relaxation algorithm presented in the section discussing algorithmic procedure.

Remarks on the solution algorithm

The diagonal elements of the Jacobian of a linearized reactor network have been derived in the previous section and are given by:

$$g_{k,k}=-q_k/V_k-u_k+\sum_{rp}\beta_{rp}\cdot\frac{\partial r_{rp}}{\partial x_i}_{ss,k} \tag{38}$$

if k corresponds to an outlet temperature and by:

$$g_{k,k}=-q_k/V_k+\sum_{rp}\nu_{rp,k}\cdot\frac{\partial r_{rp}}{\partial x_k}_{ss,k} \tag{39}$$

if k corresponds to an outlet composition. Since both of the above expressions can be made as negative as desired by appropriately adjusting q_k/V_k, the solution of a parametric problem $P(b)$ is feasible for any choice of b unless bounds are imposed on the residence times of the reactors. As a result, the matrix measure relaxation approach is also applicable to problems in which the objective is a conservative design that aims to make adequately negative eigenvalues for the Jacobian, that is, $\lambda(G)<b\ll 0$.

The components of the vector ω, introduced in the parametric problem, are derived in the previous section and involve absolute values with argument expressions related to the partial derivatives of the reaction rate. For rates of first order or for components solely consumed or produced, the sign of the arguments is predetermined and the absolute values can be dropped. If this is not the case, one can either use overestimators or assign binary variables to the sign of each argument and reformulate the parametric problem as a Mixed Integer Nonlinear Programming (MINLP) problem. Alternatively, the parametric problem can be solved with an assumed expression for each ω_k and complementary constraints for the arguments in the form: $g_{i,k}\le 0$ or $-g_{i,k}\le 0$. Then, if the marginals associated with the inequalities turn out to be nonnegative the solution is an optimal one. Otherwise, the inequalities corresponding to positive marginals should be reversed, the expressions for ω_k be accordingly modified, and a new parametric problem be solved. In terms of the type of the optimum obtained by applying the matrix measure relaxation approach in conjunction with an NLP solver, it should be noted that a global optimum is expected in the case of a convex problem and a local optimum otherwise. Because of the nonconvex type of nonlinearities involved in the mathematical formulation of the reactor network synthesis problem (Kokossis and Floudas, 1990, 1991, 1994), the final solution will always be a local optimum.

Example problems

The objective of this part is to illustrate how the matrix measure relaxation approach can be implemented for the synthesis problem of complex reactor networks. The illustrations include two example problems in which the optimal steady-state solution corresponds to an unstable equilibrium point. The formulation and the parametric problems discussed in the section on optimal design of stable systems and the application of the proposed solution algorithm results in both cases to an alternative reactor configuration that is stable and optimal.

The reaction system is given by the Van der Vusse reaction mechanism:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \quad 2A \xrightarrow{k_3} D$$

in which A represents the fresh feed component and B the desired product. Reactions 1 and 2 are of first order while reaction 3 is of second order. In terms of the system parameters, the feed is furnished with a flow rate 1 l/min, the feed concentration of A is (1 gmol/l), the kinetic constants are Arrhenius expressions of the form:

$$k_1=5.4\ 10^8\exp(15{,}840/RT) \quad s^{-1}$$

$$k_2=3.6\ 10^3\exp(7{,}920/RT) \quad s^{-1}$$

$$k_3=1.6\ 10^{10}\exp(23{,}760/RT) \quad L/mol\cdot s$$

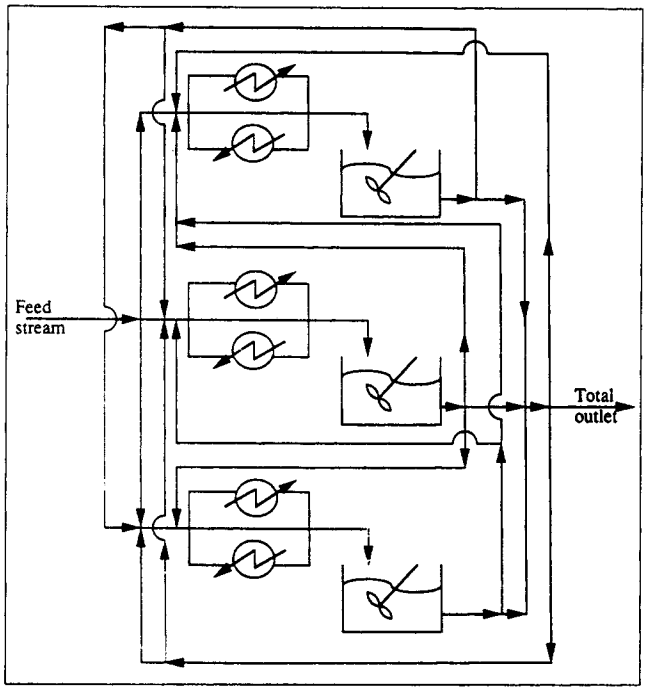

Figure 2. Reactor superstructure for example 1.

where the activation energies of the above expressions are in cal/mol and the dimensionless heats of reaction, $\gamma_i = \Delta HR_i/(\rho c_p)$, are given by:

$$\gamma_1 = -0.28,\ \gamma_2 = -0.36 \text{ and } \gamma_3 = -0.20$$

The synthesis problem is based upon a nonisothermal reactor network superstructure that consists of 3 CSTRs. The details for the generation of the superstructure and the varieties of the alternatives which are embedded in this scheme are discussed by Kokossis and Floudas (1990, 1994). In contrast to that work, the existence of the CSTRs is not treated as an optimization variable (that is, all CSTRs participate in the optimal configuration) and the synthesis problem is formulated as a Nonlinear Programming (NLP) problem. The algorithmic parameter, b, of the matrix measure relaxation approach is updated based upon a bisection search, and the state variables of the dynamical system represent the deviations of the outlet concentrations of the reactants and the outlet reactor temperatures of the reactors. Since the matrix of the stoichiometric coefficients is of rank 2, the Jacobian of the linearized network results in a 9 by 9 matrix the elements of which are given in the Appendix B.

Example 1. The system is fed with a stream of temperature 330°K and the reactors have residence times within 20–100 s. All temperatures are allowed in the range 300–360° while the interconnecting streams are within 0.1–100 L/min. From the assumed superstructure, given in Figure 2, the reactors operate adiabatically and thermal control is available by heating or cooling the inlets of the reactors.

The reactor configuration that optimizes the yield of B is given in Figure 3. The reactors are arranged in series, the first and third are precooled from 330 to 297 K and the second CSTR is preheated from 300 to 305 K. The reactor outlet

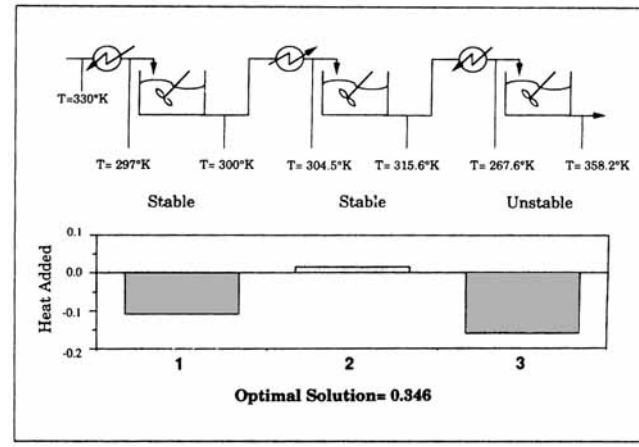

Figure 3. Unstable optimal solution of example 1.

temperatures along the cascade are 300, 315, and 358 K while the optimal yield is found 0.346. The steady state associated with the third CSTR, however, is unstable and so is the overall reactor configuration. The result can also be checked through the eigenvalues of the Jacobian for the linearized network.

The matrix measure relaxation approach is applied to this system for $\epsilon_1 = \epsilon_2 = 10^{-2}$. The steps of the algorithmic procedure are given in Figure 4. The first plot of the figure provides the maximum and the minimum real part of the eigenvalues of the Jacobian evaluated at the solution of each parametric problem. The second plot gives the levels of z^{lo} and z^{up} at each iteration. Convergence is achieved whenever the two curves of the graph meet and this requires a total of seven iterations. The optimal stable solution is given in Figure 5. In this solution, all CSTRs are precooled and the outlet reactor temperatures along the cascade are found to be 310, 300, and 301 K. The yield associated with this configuration is 0.118.

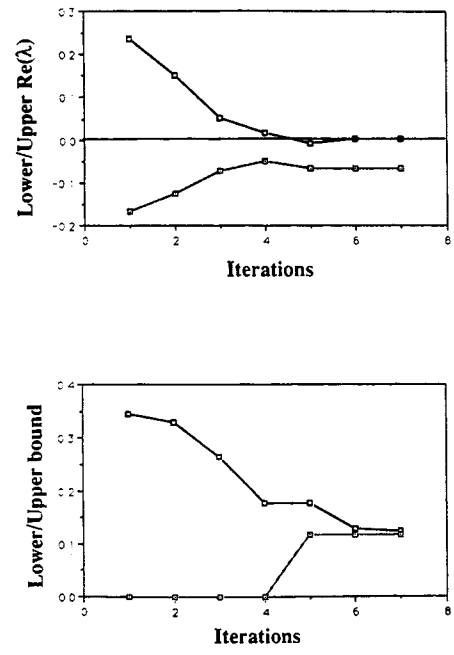

Figure 4. Iterative procedure for example 1.

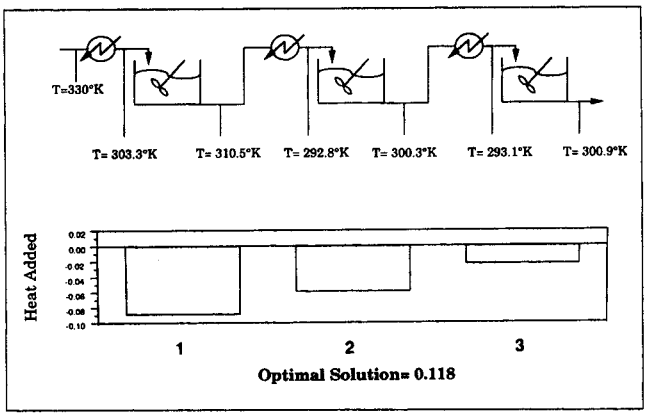

Figure 5. Stable optimal solution of example 1.

Example 2. The reactor system is furnished with a feed stream of temperature 300°K. The residence times of the reactors are within 0.1–20 s while all temperatures are allowed in the range 360–396 K. In contrast to the previous example the reactors operate nonadiabatically and the assumed superstructure is given in Figure 6.

The objective of the synthesis problem is given by:

$$f(x_B^{out}, Q) = x_B^{out} - p \cdot \Sigma Q_i^2$$

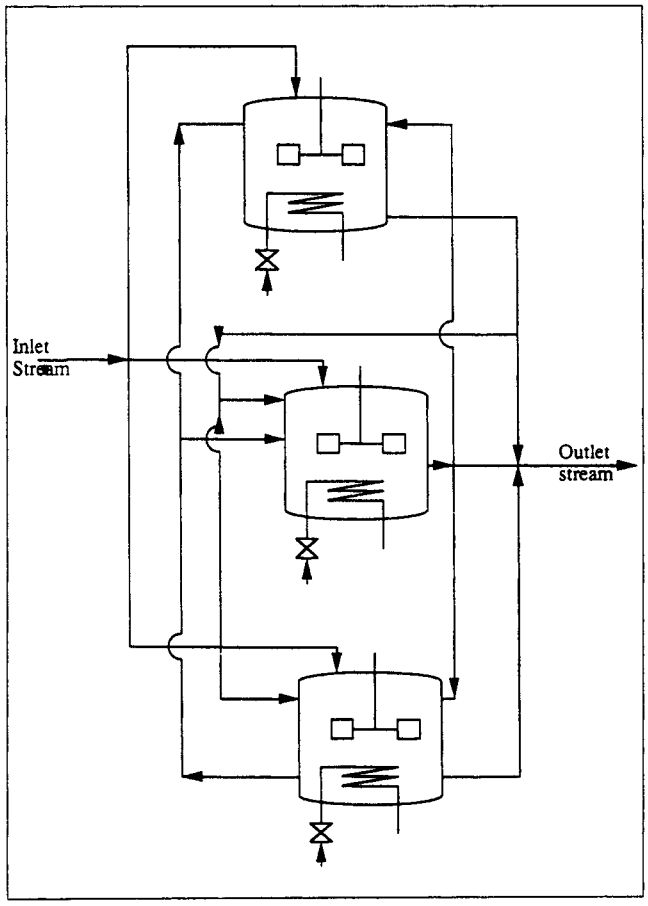

Figure 6. Reactor superstructure of example 2.

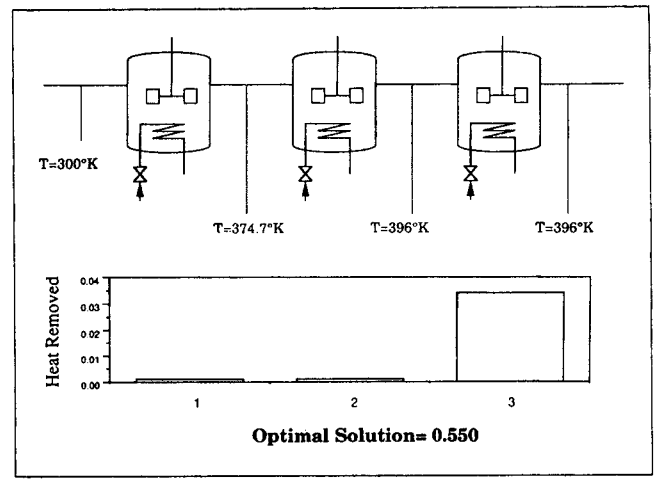

Figure 7. Unstable optimal solution of example 2.

where x^{out} is the outlet concentration of B from the reactor network, Q_i the heat loads at each reactor, and p, a penalty parameter set to 0.8.

The solution of the optimization problem without stability considerations results in the reactor configuration of Figure 7. In the optimal solution the CSTRs are arranged in series; the first and second reactor operate almost adiabatically while the third CSTR is precooled and operates nonadiabatically and maintains an outlet temperature equal to 396 K. The optimal configuration has an objective function equal to 0.55 but it is unstable.

The application of the matrix measure relaxation approach is based upon the same convergence criteria with example 1, and the steps of the solution procedure are given in Figure 8. The optimal and stable configuration is given in Figure 9 and is quite different from the unstable configuration of Figure 7. First the cooling strategy along the cascade has been reversed and most of the heat is removed from the first CSTR. Secondly, the reactor configuration is structurally different and it features a recycle from the second to the first CSTR. The outlet temperatures along the cascade are found to be 360, 378 and 380 K. The optimal solution associated with this configuration results to an objective equal to 0.373.

Note that in the two considered examples the optimal solutions found by introducing the stability criterion exhibit lower yields compared to the unstable solutions. This can be attributed to the conservative nature of the measure of stability used in this work.

Conclusions

A systematic methodology has been presented for the optimal design of stable systems. The methodology is based upon the formulation of a parametric problem that bounds the optimal stable solution to which it converges within a number of iterations. When extended to the synthesis problem of reactor networks, the approach is able to couple the optimization problem with stability concerns even in cases where the number of reactors is large and the reaction mechanism is described by a general complex reaction scheme. Furthermore, since at the synthesis level the reactor network represents an exhaustive superposition of the existing structural and operational alter-

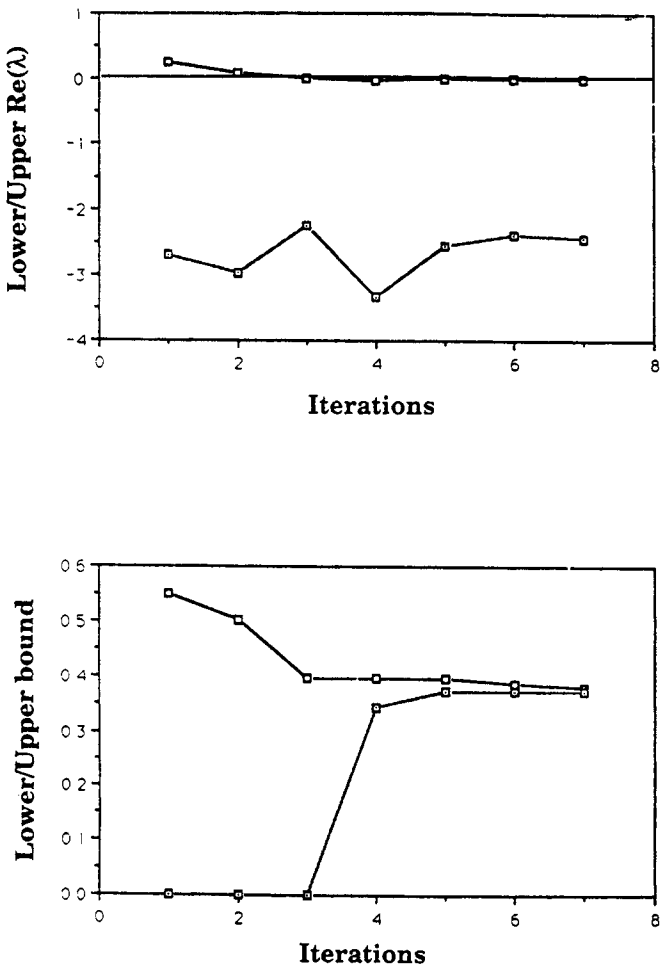

Figure 8. Iterative procedure for example 2.

natives, the approach fully exploits these alternatives and coordinates a weighted optimal search that improves the objective and accommodates a stable reactor network.

In reference to chemical engineering processes, the approach can be implemented to the reactor design problem so that to exclude unstable operating points or study structural and operational alternatives that may compensate for stability concerns. Since it is not limited to specific or small dynamical systems, the methodology can handle equally well cases of isothermal, adiabatic, or nonisothermal reactors, cases of interconnected reactors processing complex reaction schemes, or even complex reactor network superstructures that provide complete representations of the existing design alternatives.

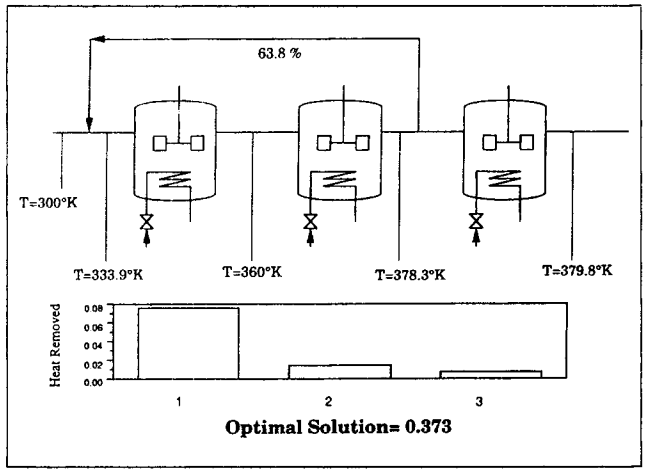

Figure 9. Stable optimal solution of example 2.

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Appendix A: Proof of Theorem 3

(a) By definition:

$$z(\boldsymbol{b}) = \min_{y \in D(b)} f(y)$$

where

$$\boldsymbol{D}(\boldsymbol{b}) = \{ y \in F: \mu[G(y)] < \boldsymbol{b} \}$$

Let the n-dimensional vectors $\boldsymbol{b}_1 = [b_1^1, b_2^1, \ldots, b_n^1]^T$ and $\boldsymbol{b}_2 = [b_1^2, b_2^2, \ldots, b_n^2]^T$ with $b_k^1 \le b_k^2$, $k = 1, 2, \ldots, n$. Then, $\boldsymbol{D}(\boldsymbol{b}_1) \subset \boldsymbol{D}(\boldsymbol{b}_2)$ and:

$$h(\boldsymbol{b}_1) = \min_{y \in D(b_1)} f(y) \ge \min_{y \in D(b_2)} f(y) = h(\boldsymbol{b}_2)$$

Therefore, $z(\boldsymbol{b})$ is a monotonically nonincreasing function.

(b) By definition $S \subseteq F$ and:

$$f(\boldsymbol{x}^*, \boldsymbol{p}^*) = \min_{y \in S} f(y) \ge \min_{y \in F} f(y) = z^{lo}$$

Since $\boldsymbol{F}$ is compact and $\boldsymbol{D}(\boldsymbol{b}) \subseteq \boldsymbol{F}\ \forall \boldsymbol{b} \in \Re^n$,

$$h(\boldsymbol{b}) = \min_{y \in D(b)} f(y) \ge \min_{y \in F} f(y) = z^{lo}$$

For $\boldsymbol{b}_n \to \infty$, the sequence $h(\boldsymbol{b}_n)$ is decreasing and bounded by z^{lo}. Therefore, the sequence converges and $\exists z_\infty \in \Re$ such that:

$$z_\infty = \lim_{b \to \infty} h(\boldsymbol{b})$$

Furthermore, $\lim_{b \to \infty} \boldsymbol{D}(\boldsymbol{b}) = \boldsymbol{F}$ and:

$$z_\infty = \lim_{b \to \infty} \min_{y \in D(b)} f(y) = \min_{y \in \lim_{b \to \infty} D(b)} f(y) = \min_{y \in F} f(y) = z^{lo}$$

Appendix B: Jacobian Matrix of Example Problems 1 and 2

Let k denote a particular CSTR of the superstructure and the following symbols stand for:

- $m_{i,k}$ the interconnecting stream from reactor i to reactor k

- $x_{o,k}$ the dimensionless steady-state reactor temperature
- u_k the dimensionless heats of reaction
- V_k the reactor volume
- r^k_{rp} the rp reaction rate
- $c_{A,k}$, $c_{B,k}$ the outlet concentrations of A and B
- τ_k the residence time of the reactor.

The Jacobian of example 1 and 2 is then given by the following 9×9 matrix:

$$\left\{\left\{-\frac{r_1^1}{c_{A,1}}-\frac{2r_3^1}{c_{A,1}}-\frac{1}{\tau_1},\ 0,\ \frac{-26.573r_1^1}{x_{o,1}^2}-\frac{13.286r_3^1}{x_{o,1}^2},\ \frac{m_{2,1}}{V_1},\ 0,\ 0,\ \frac{m_{3,1}}{V_1},\ 0,\ 0\right\},\right.$$

$$\left\{\frac{r_1^1}{c_{A,1}},\ -\frac{r_2^1}{c_{B,1}}-\frac{1}{\tau_1},\ \frac{26.573r_1^1}{x_{o,1}^2}-\frac{39.859r_2^1}{x_{o,1}^2},\ 0,\ \frac{m_{2,1}}{V_1},\ 0,\ 0,\ \frac{m_{3,1}}{V_1},\ 0\right\},$$

$$\left\{\frac{0.28r_1^1}{c_{A,1}}+\frac{0.4r_3^1}{c_{A,1}},\ \frac{0.36r_2^1}{c_{B,1}},\ -\frac{1}{\tau_1}+\frac{7.44r_1^1+14.349r_2^1+2.6572r_3^1}{x_{o,1}^2}-u_1,\ 0,\ 0,\ \frac{m_{2,1}}{V_1},\ 0,\ 0,\ \frac{m_{3,1}}{V_1}\right\},$$

$$\left\{\frac{m_{1,2}}{V_2},\ 0,\ 0,\ -\frac{r_1^2}{c_{A,2}}-\frac{2r_3^2}{c_{A,2}}-\frac{1}{\tau_2},\ 0,\ \frac{-26.573r_1^2}{x_{o,2}^2}-\frac{13.286r_3^2}{x_{o,2}^2},\ \frac{m_{3,2}}{V_2},\ 0,\ 0\right\},$$

$$\left\{0,\ \frac{m_{1,2}}{V_2},\ 0,\ \frac{r_1^2}{c_{A,2}},\ -\frac{r_2^2}{c_{B,2}}-\frac{1}{\tau_2},\ \frac{26.573r_1^2}{x_{o,2}^2}-\frac{39.859r_2^2}{x_{o,2}^2},\ 0,\ \frac{m_{3,2}}{V_2},\ 0\right\},$$

$$\left\{0,\ 0,\ \frac{m_{1,2}}{V_2},\ \frac{0.28r_1^2}{c_{A,2}}+\frac{0.4r_3^2}{c_{A,2}},\ \frac{0.36r_2^2}{c_{B,2}},\ -\frac{1}{\tau_2}+\frac{7.44r_1^2+14.349r_2^2+2.6572r_3^2}{x_{o,2}^2}-u_2,\ 0,\ 0,\ \frac{m_{3,2}}{V_2}\right\},$$

$$\left\{\frac{m_{1,3}}{V_3},\ 0,\ 0,\ \frac{m_{2,3}}{V_3},\ 0,\ 0,\ -\frac{r_1^3}{c_{A,3}}-\frac{2r_3^3}{c_{A,3}}-\frac{1}{\tau_3},\ 0,\ \frac{-26.573r_1^3}{x_{o,3}^2}-\frac{13.286r_3^3}{x_{o,3}^2}\right\},$$

$$\left\{0,\ \frac{m_{1,3}}{V_3},\ 0,\ 0,\ \frac{m_{2,3}}{V_3},\ 0,\ \frac{r_1^3}{c_{A,3}},\ -\frac{r_2^3}{c_{B,3}}-\frac{1}{\tau_3},\ \frac{26.573r_1^3}{x_{o,3}^2}-\frac{39.859r_2^3}{x_{o,3}^2}\right\},$$

$$\left.\left\{0,\ 0,\ \frac{m_{1,3}}{V_3},\ 0,\ 0,\ \frac{m_{2,3}}{V_3},\ \frac{0.28r_1^3}{c_{A,3}}+\frac{0.4r_3^3}{c_{A,3}},\ \frac{0.36r_2^3}{c_{B,3}},\ -\frac{1}{\tau_3}+\frac{7.44r_1^3+14.349r_2^3+2.6572r_3^3}{x_{o,3}^2}-u_3\right\}\right\}$$

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