Recent Advances in Global Optimization for Process Synthesis, Design and Control : Enclosure of All Solutions

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Abstract–Recent advances in global optimization for process synthesis, design and control are discussed. After a review of the chemical engineering contributions, we focus on the enclosure of all solutions of nonlinear constrained systems of equations. Important theoretical results are presented accompanied with computational studies on the enclosure of multiple steady states and all homogeneous azeotropes.

1 Introduction and Review

A significant effort has been expended in the last four decades toward theoretical and algorithmic studies of applications that arise in Chemical Engineering Process Design, Process Synthesis, Process Control, as well as in Computational Chemistry and Molecular Biology. In the last decade we have experienced a dramatic growth of interest in Chemical Engineering for new methods of global optimization and their application to important engineering, as well as computational chemistry and molecular biology problems.

Contributions from the chemical engineering community to the area of global optimization can be traced to the work of Stephanopoulos and Westerberg (1975), and Westerberg and Shah (1978). Renewed interest in seeking global solutions was motivated from the work of Floudas *et al.* (1989). The first exact primal-dual global optimization approach was proposed by Floudas and Visweswaran (1990), (1993) and its features were explored for quadratically constrained and polynomial problems in the work of Visweswaran and Floudas (1990), (1992), (1993). Swaney (1990) proposed a branch and bound global optimization approach and more recently Quesada and Grossmann (1993), (1995) combined convex underestimators in a branch and bound framework for linear fractional and bilinear programs. Manousiouthakis and Sourlas (1992) proposed a reformulation to a series of reverse convex problems, and Tsirukis and Reklaitis (1993) proposed a feature extraction algorithm for constrained global optimization. Maranas and Floudas (1992), (1993), (1994a), (1994b) proposed a novel branch and bound method combined with a difference of convex functions transformation for the global optimization of molecular conformation problems that arise in computational chemistry. A very important theoretical advance has been made by Liu and Floudas (1993), (1995), (1996) who showed that the GOP can be applied to very general classes of NLPs where the objective function and constraints are twice-continuously differentiable. Vaidyanathan and El-Halwagi (1994) proposed an interval analysis based global optimization method. In a series of papers, McDonald and Floudas (1994), (1995a), (1995b), (1995c) addressed the fundamental problems of (i)minimization of the Gibbs free energy and (ii) the tangent plane stability criterion that arise in phase and chemical reaction equilibrium as global optimization problems for the first time. They proposed decomposition based approaches for biconvex problems that result from the use of the NRTL equation, and branch and bound approaches for the UNIQUAC, UNIFAC, ASOG, and TK-Wilson. Psarris and Floudas (1995) proposed a global optimization approach based on the GOP approach for the robust stability of control systems under real parametric uncertainty. Ryoo and Sahinidis (1995) suggested the application of reduction tests within the framework of branch and bound methods and they proposed a branch and reduce global optimization approach (Ryoo and Sahinidis (1996)). Dorneigh and Sahinidis (1995) proposed a global optimization approach for the chip layout and compaction problem. Androulakis *et al.* (1995) proposed the global optimization method αBB which addresses general continuous optimization problems with nonconvexities in the objective function and/or constraints. This approach classifies the nonconvexities as special structure (e.g., bilinear, signomial, univariate) or generic structure and is based on convex relaxations and a branch and bound framework. Maranas and Floudas (1995) proposed a new approach for enclosing all ϵ-feasible solutions of nonlinearly constrained systems of equations. This approach transforms the problem into a min-max form and corresponds to enclosing all multiple global optima via the αBB global optimization approach.

The books of Floudas and Pardalos (1996) and Grossmann (1996) contain a number of chemical engineering contributions up to 1996 (not discussed here due to space limitations), the review paper of Floudas (1997) presents an overview of chemical engineering contributions and the advances in global optimization based on the decomposition approach GOP, the generalized geometric programming, and the αBB approach, while the forthcoming book of Floudas (2000) provides an up-to-date account of the developments in the area of global optimization.

Maranas and Floudas (1997) proposed a global optimization approach for generalized geometric programming problems that have many applications in robust control and engineering design problems. activity coefficient models. McDonald and Floudas (1997) proposed the combination of the Gibbs free energy minimization problem with the stability criterion problem, and developed a special purpose program GLOPEQ, and performed an extensive computational study on difficult phase equilibrium problems. Harding *et al.* (1997) proposed novel formulations and global optimization methods for the enclosure of all homogeneous azeotropes. This approach offers a theoretical guarantee of enclosing all homogeneous azeotopes and it was applied to a variety of activity coefficient models. Androulakis *et al.* (1997a) proposed a novel global optimization approach based on atomistic level modeling and the αBB principles for the structure prediction of oligopeptides. Androulakis *et al.* (1997b) proposed a decomposition based global optimization approach for the peptide docking problem of aminoacids into the binding sites of the HLA-DR1 protein. Harding and Floudas (1997) proposed novel global optimization approaches for the batch design under uncertainty of multiproduct and multipurpose plants. These approaches are based on the exact calculation of the α parameters within the αBB global optimization framework and they result in the tightest possible underestimators. Epperly *et al.* (1997) proposed a global optimization approach for stochastic batch design problems that is based on a reduction of the number of variables needed for branching as suggested in their reduced space branch and bound approach (Epperly and Pistikopoulos (1997)). Sriniwas and Arkun (1997) introduced a global optimization approach based on the GOP principles for the nonlinear model predictive control problems with polynomial ARX models. VanAntwerp *et al.* (1997) introduced a global optimization approach based on branch and bound for the design of a robust controller to time-varying nonlinear plant perturbations. Smith and Pantelides (1997) studied further their reformulation/spatial branch and bound approach for the global optimization of MINLP problems.

Klepeis *et al.* (1998), and Klepeis and Floudas (1998) proposed new global optimization approaches for the structure prediction of solvated peptides using the area and the volume accessible to the solvent models. A review of the global optimization activities in the areas of protein folding and peptide docking can be found in Floudas *et al.* (1998). Esposito and Floudas (1998) proposed the first global optimization method for the parameter estimation and data reconcilliation of nonlinear algebraic models using the principles of the αBB approach. McKinnon and Mongeau (1998) proposed a generic global optimization approach for the phase and chemical reaction equilibrium problem that is based on interval analysis and combines the stability criterion with the minimization of the Gibbs free energy. Hua *et al.* (1998) applied an interval analysis method for the phase stability computations of binary and ternary mixtures using equation of state models. Maier *et al.* (1998) applied an interval analysis based approach for the enclosure of homogeneous azeotropes. They employed the formulations proposed by Harding *et al.* (1997) and studied systems with activity coefficient and equation of state models. Shectman and Sahinidis (1998) proposed a finite global optimization method for separable concave problems. Yamada and Hara (1998) proposed a global optimization approach based on the triangle covering for H-infinity control with constant diagonal scaling. Androulakis and Floudas (1998) studied the parallel computation issues that arise using the αBB global optimization approach. Adjiman *et al.* (1998a) proposed several new rigorous methods for the calculation of the α parameters for (i) uniform diagonal shift of the hessian matrix and (ii) non-uniform diagonal shift of the hessian matrix, and they established their potential trade-offs. Adjiman *et al.* (1998b) presented the detailed implementation of the αBB approach and computational studies in process design problems such as heat exchanger networks, reactor-separator networks, and batch design under uncertainty. Westerlund *et al.* (1998) proposed an extended cutting plane approach for the global optimization of pseudoconvex MINLP problems. Zamora and Grosmmann (1998) proposed a hybrid branch-and-bound and outer approximation method for the global optimization of heat exchanger networks with no stream splits. Adjiman *et al.* (1998d) proposed two novel global optimization approaches for nonconvex mixed-integer nonlinear programming problems. The first approach is for separable continuous and integer domains while the second approach addresses general mixed-integer nonlinear problems.

2 Enclosure of All Solutions

The enclosure of all solutions of nonlinear constrained systems of equations is regarded as a very challenging task in applied mathematics, engineering and sciences. Representative applications include (i) the identification of potential multiplicities of exothermic reactions occurring in adiabatic CSTR's; (ii) the solution of cubic equations in PVT calculations for the vapor, liquid and metastable state specific volumes; (iii) evaluation of multiple–steady states in certain types of reaction networks; (iv) the identification of multiple solutions for porous catalysts effectiveness factors in exothermic reactions; (v) the solution of (un)constrained simulation problems in steady–state flowsheet modelling; (vi) the identification of equilibrium points in (un)reacting multiphase systems such as multiple miscibility gaps in liquid–

liquid phase equilibria; (vii) the prediction of all homogeneous, heterogeneous and reactive azeotropes, as well as eutectic points at some temperature or pressure for given activity coefficient models; (viii) the location of all multiple steady states of individual distillation columns and of interlinked separation systems; (ix) the prediction of multiple steady–states in various complex reactor systems; and (x) the prediction of multiplicities occurring in fluid mechanics when solving nonlinear boundary value problems in ODE's.

There exists a large body of literature on methods for solving systems of equations. These approaches fall within three broad classes: (i) Newton and quasi–Newton type methods; (ii) homotopy continuation type (embedding) methods; (iii) Interval–Newton methods; and (iv) deterministic global optimization methods.

Newton and quasi–Newton type methods and their modifications achieve superlinear convergence only when they are well within the neighborhood of the solution. However, these methods are likely to fail if the initial guess is poor or if singular points are encountered.

The second class of methods are the *embedding methods* also known as *continuation, homotopy continuation, or incremental loading*. A comprehensive review of the extensive literature in this area can be found in Garcia and Zangwill (1981). Application of the homotopy ideas for a variety of chemical engineering problems has been very extensive (Salgovic *et al.*, 1981; Bhargava and Hlavacek, 1984; Wayburn and Seider, 1983; Chavez *et al.*, 1986; Hlavacek, 1985; Byrne and Baird, 1985; Bekiaris *et al.*, 1993). A problem common to all homotopy variants is that variable bounds and inequality constraints cannot be handled directly. More importantly, mathematical guarantees that all solutions will be found exist only in special cases (e.g., polynomial systems with no constraints).

Interval–Newton methods can enclose all solutions of nonlinear systems of equations lying within certain variable bounds. They do so by applying the classical Newton-like iterative methods on interval variables rather than variables coupled with a generalized bisection strategy. Interval computations are discussed in detail in Neumaier (1990) and Hansen (1992). A version of the basic Interval–Newton method has been implemented into the program INTBIS by Kearfott and Novoa (1990) which is coupled with a portable interval standard function library INTLIB by Kearfott *et al.* (1994). Seader and Kumar (1994) studied the presence of multiple steady–states in certain process simulation examples and Schnepper and Stadtherr (1996) based on a parallel implementation addressed a number of process flowsheeting problems. McKinnon and Mongeau (1998), Hua *et al.* (1996), and Hua *et al.* (1998), applied interval analysis methods for the phase and chemical reaction equilibrium problems, while Maier *et al.* (1998) studied the enclosure of all homogeneous azeotropes based on the formulations proposed by Harding *et al.* (1997). The applicability of Interval Newton methods to general nonlinear functions comes at an expense. Because no specific structure of the individual expressions participating in the nonlinear equations is analyzed, the obtained lower/upper bounds on these nonlinear expressions tend to be fairly loose.

Deterministic global optimization approaches for enclosing all solutions of nonlinear constrained systems of equations are based on a branch and bound framework which explores the entire space and therefore they can provide guarantees for enclosing all solutions (see Maranas and Floudas (1995)). The fundamental difference between the deterministic global optimization approaches and Interval–Newton methods is that while the latter bounds functions with scalars, in the deterministic branch and bound global optimization approaches, we exploit the mathematical structure of the problem, so as to underestimate the nonconvex functions by tight convex functions resulting in much tighter bounds.

2.1 Problem Definition

The problem of enclosing all solutions of a nonlinear system of equations subject to inequality constraints and variable bounds is formulated as:

$$\begin{array}{c} h_j(\boldsymbol{x}) = 0, \;\; j \in \mathcal{N}_E \\ g_k(\boldsymbol{x}) \leq 0, \;\; k \in \mathcal{N}_I \\ \boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U \end{array} \tag{1}$$

where $\mathcal{N}_E$ is the set of equalities, $\mathcal{N}_I$ the set of inequality constraints, and $\boldsymbol{x}$ the vector of variables.

Note that in formulation (1), the total number of variables is allowed to be different than the total number of equalities so as neither the existence nor the uniqueness of a solution of (1) is postulated. Therefore, overspecified and underspecified systems are included in the present investigations. Note that a number of important problems naturally arise as special instances of formulation (1). Eliminating all inequality constraints, (1) corresponds to a system of nonlinear equations. Eliminating all equality constraints (1) checks the existence of feasible points for the given inequality constraint set.

Introducing a single slack variable s, formulation (1) can be written as the following optimization problem (2):

$$\begin{array}{rlll} \min_{\boldsymbol{x}, s \geq 0} & s & & \\ \text{s.t.} \;\; h_j(\boldsymbol{x}) - s & \leq & 0, & j \in \mathcal{N}_E \\ -h_j(\boldsymbol{x}) + s & \leq & 0, & j \in \mathcal{N}_E \\ g_k(\boldsymbol{x}) & \leq & 0, & k \in \mathcal{N}_I \\ \boldsymbol{x}^L \leq \boldsymbol{x} & \leq & \boldsymbol{x}^U. & \end{array} \tag{2}$$

Notice that there is a one to one correspondence between multiple global minima $(\boldsymbol{x}^*, s^*)$ of (2) for which $s^* = 0$ and solutions of (1). This means that if the global minimum of (2) involves a nonzero slack variable s^* then the original problem (1) has no solutions. Note that, unless the functions $h_j(\boldsymbol{x})$ are *linear* and $g_k(\boldsymbol{x})$ are *convex*, formulation (2) corresponds to a *nonconvex* optimization problem. This implies that if a local optimization approach is used to solve (2) one might miss some of the multiple global minima of (2) or even erroneously deduce that there are no solutions for (1).

A lower bound on the solution of (2) is found by first replacing each nonconvex constraint in (2) with a convex underestimation of it and the subsequent solution of the convex relaxation of (2). This approach naturally partitions the constraints of formulation (2) into convex constraints for which no relaxation is required and nonconvex ones. This partitioning yields the following alternative formulation (3):

$$\begin{array}{lll} \min\limits_{\boldsymbol{x}, s \geq 0} & s & \\ \text{s.t.} \;\; h_j^{nonc}(\boldsymbol{x}) - s & \leq & 0, \; j \in \mathcal{N}_{noncE} \\ -h_j^{nonc}(\boldsymbol{x}) + s & \leq & 0, \; j \in \mathcal{N}_{noncE} \\ g_k^{nonc}(\boldsymbol{x}) & \leq & 0, \; k \in \mathcal{N}_{noncI} \\ h_j^{lin}(\boldsymbol{x}) & = & 0, \; j \in \mathcal{N}_{linE} \\ g_k^{conv}(\boldsymbol{x}) & \leq & 0, \; j \in \mathcal{N}_{convI} \\ & \boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U, & \end{array} \tag{3}$$

where $\mathcal{N}_{noncE}, \mathcal{N}_{linE}$ are the sets of nonconvex and linear equality constraints respectively, and $\mathcal{N}_{noncI}, \mathcal{N}_{convE}$ are the sets of nonconvex and convex inequality constraints,

$$\mathcal{N}_E = \mathcal{N}_{noncE} \cup \mathcal{N}_{linE}, \;\; \mathcal{N}_I = \mathcal{N}_{noncI} \cup \mathcal{N}_{convI}.$$

A convex relaxation (4) of (3) of the form:

$$\begin{array}{lll} \min\limits_{\boldsymbol{x}, s \geq 0} & s & \\ \text{s.t.} \;\; \hat{h}_{+,j}^{nonc}(\boldsymbol{x}) - s & \leq & 0, \; j \in \mathcal{N}_{noncE} \\ \hat{h}_{-,j}^{nonc}(\boldsymbol{x}) + s & \leq & 0, \; j \in \mathcal{N}_{noncE} \\ \hat{g}_k^{nconc}(\boldsymbol{x}) & \leq & 0, \; k \in \mathcal{N}_{noncI} \\ h_j^{lin}(\boldsymbol{x}) & = & 0, \; j \in \mathcal{N}_{linE} \\ g_k^{conv}(\boldsymbol{x}) & \leq & 0, \; j \in \mathcal{N}_{convI} \\ & \boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U, & \end{array} \tag{4}$$

can be obtained by replacing the original nonconvex functions

$$h_j^{nonc}(\boldsymbol{x}), \;\; -h_j^{nonc}(\boldsymbol{x}), \;\; g_k^{nonc}(\boldsymbol{x})$$

with some convex tight lower bounding functions

$$\hat{h}_{+,j}^{nonc}(\boldsymbol{x}), \;\; \hat{h}_{-,j}^{nonc}(\boldsymbol{x}), \;\; \hat{g}_k^{nonc}(\boldsymbol{x}).$$

These lower bounding functions $\hat{h}_{+,j}^{nonc}(\boldsymbol{x})$,$\hat{h}_{-,j}^{nonc}(\boldsymbol{x})$, $\hat{g}_k^{nonc}(\boldsymbol{x})$ must satisfy the following properties :

Property 2.1 $\hat{h}_{+,j}^{nonc}(\boldsymbol{x})$, $\hat{h}_{-,j}^{nonc}(\boldsymbol{x})$, and $\hat{g}_k^{nonc}(\boldsymbol{x})$ be convex $\forall \, \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$.

Property 2.2 $h_{+,j}^{nonc}(\boldsymbol{x}) \geq \hat{h}_j^{nonc}(\boldsymbol{x})$, $h_{-,j}^{nonc}(\boldsymbol{x}) \geq -\hat{h}_j^{nonc}(\boldsymbol{x})$, and $g_k^{nonc}(\boldsymbol{x}) \geq \hat{g}_k^{nonc}(\boldsymbol{x})$, $\forall \, \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$.

Property 2.3 $\forall \; \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$ and $\epsilon > 0$, $\exists \; [\boldsymbol{x}^L, \boldsymbol{x}^U] \subseteq [\boldsymbol{x}^L, \boldsymbol{x}^U]$ with $\delta(\epsilon) = \|\boldsymbol{x}^U - \boldsymbol{x}^L\|_2^{1/2} > 0$ such that

$$\max_{\boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]} \left(h_j^{nonc}(\boldsymbol{x}) - \hat{h}_{+,j}^{nonc}(\boldsymbol{x}) \right) < \epsilon,$$

$$\max_{\boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]} \left(-h_j^{nonc}(\boldsymbol{x}) - \hat{h}_{-,j}^{nonc}(\boldsymbol{x}) \right) < \epsilon,$$

$$\max_{\boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]} \left(g_k^{nonc}(\boldsymbol{x}) - \hat{g}_k^{nonc}(\boldsymbol{x}) \right) < \epsilon.$$

Remark 2.1 Property 2.3 requires that the maximum separation between the nonconvex function and its tight convex lower bounding function, defined inside some rectangular region, must go to zero

$$\lim_{\delta \to 0^+} \epsilon = 0.$$

as the size of the rectangular domain approaches zero ($\delta = 0$). This is important for proving finite $\epsilon-$convergence. The order $\mathcal{O}(\epsilon) = \mathcal{O}(\delta^n)$ with which ϵ approaches zero is important because it determines the speed of convergence.

2.2 Convex Lower Bounding

An efficient convex lower bounding of the nonconvex functions appearing in formulation (3) is central to the design of the deterministic global optimization approach for enclosing all solutions of nonlinear constrained systems of equations. The first important step in the convexification strategy is the decomposition of each nonlinear function into a sum of terms belonging to one of several categories: linear, bilinear, trilinear, fractional, fractional trilinear, convex, univariate concave or general nonconvex. It is also possible to construct customized underestimators for other mathematical structures such as signomial expressions, as shown by Maranas and Floudas (1997). In constructing a convex underestimator for the overall function, it is first noted that the linear and convex terms do not require any transformation. The convex envelope of the bilinear, fractional, and univariate concave terms can be constructed by following simple rules. For a more detailed exposition the reader is directed to Maranas and Floudas (1995,1997) Adjiman et al. (1998a,b), and the forthcoming book of Floudas (2000).

Bilinear Terms : In the case of a bilinear term xy, McCormick (1976), Al-Khayyal and Falk (1983) showed that the tightest convex lower bound over the domain $[x^L, x^U] \times [y^L, y^U]$ is obtained by introducing a new variable w_B which replaces every occurrence of xy in the problem and satisfies :

$$\begin{array}{rcl} w_B & \geq & x^L y + y^L x - x^L y^L, \\ w_B & \geq & x^U y + y^U x - x^U y^U, \\ w_B & \leq & x^U y + y^L x - x^U y^L, \\ w_B & \leq & x^L y + y^U x - x^L y^U. \end{array} \tag{5}$$

Fractional Terms : Fractional terms of the form x/y are underestimated by introducing a new variable w_F and two new constraints (Maranas and Floudas, 1995) which depend on the sign of the bounds on x.

$$\begin{array}{rcl} w_F & \geq & \left\{ \begin{array}{ll} x^L/y + x/y^U - x^L/y^U & \text{if } x^L \geq 0 \\ x/y^U - x^L y/y^L y^U + x^L/y^L & \text{if } x^L < 0 \end{array} \right. \\ w_F & \geq & \left\{ \begin{array}{ll} x^U/y + x/y^L - x^U/y^L & \text{if } x^U \geq 0 \\ x/y^L - x^U y/y^L y^U + x^U/y^U & \text{if } x^U < 0 \end{array} \right. \end{array} \tag{6}$$

Univariate Concave Terms : Univariate concave functions are underestimated by their linearization at the lower bound of the variable range. Thus the convex envelope of the concave function $ut(x)$ over $[x^L, x^U]$ is the linear function of x:

$$ut(x^L) + \frac{ut(x^U) - ut(x^L)}{x^U - x^L}(x - x^L). \tag{7}$$

General Nonconvex Terms : For the most general nonconvexities, a slightly modified version of the underestimator proposed by Maranas and Floudas (1994b) is used. A function $f(\boldsymbol{x}) \in \mathcal{C}^2(\Re^n)$ is underestimated over the entire domain $[\boldsymbol{x}^L, \boldsymbol{x}^U]$ by the function $\mathcal{L}(\boldsymbol{x})$ defined as

$$\mathcal{L}(\boldsymbol{x}) = f(\boldsymbol{x}) + \sum_{i=1}^{n} \alpha_i (x_i^L - x_i)(x_i^U - x_i) \tag{8}$$

where the α_i's are positive scalars.

Since the summation term in Equation (8) is negative over the entire region $[\boldsymbol{x}^L, \boldsymbol{x}^U]$, $\mathcal{L}(\boldsymbol{x})$ is a guaranteed underestimator of $f(\boldsymbol{x})$. Furthermore, since the quadratic term is convex, all nonconvexities in the original function $f(\boldsymbol{x})$ can be overpowered given sufficiently large values of the α_i parameters: $\mathcal{L}(\boldsymbol{x})$ is therefore a *valid convex underestimator*. A useful convexity condition is derived by noting that $H_{\mathcal{L}}(\boldsymbol{x})$ is related to the Hessian matrix $H_f(\boldsymbol{x})$ of $f(\boldsymbol{x})$ by

$$H_{\mathcal{L}}(\boldsymbol{x}) = H_f(\boldsymbol{x}) + 2\ \Delta, \tag{9}$$

where Δ is a diagonal matrix whose diagonal elements are the α_i's. Δ is referred to as the *diagonal shift matrix*, since the addition of the quadratic term to the function $f(\boldsymbol{x})$, as shown in Equation (8), corresponds to the introduction of a *shift* in the diagonal elements of its Hessian matrix $H_f(\boldsymbol{x})$. The following theorem can then be used to ensure that $\mathcal{L}(\boldsymbol{x})$ is indeed a convex underestimator:

Theorem 2.2.1 *$\mathcal{L}(\boldsymbol{x})$, as defined in Equation (8), is convex if and only if $H_f(\boldsymbol{x}) + 2\ \Delta = H_f(\boldsymbol{x}) + 2\ \mathrm{diag}\,(\alpha_i)$ is positive semi-definite for all $\boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$.*

A number of deterministic methods have been devised in order to automatically identify an appropriate diagonal shift matrix (Adjiman and Floudas, 1996; Adjiman et al. (1998a,b). The key idea is to introduce the interval hessian $[H_f]$ such that $H_f(\boldsymbol{x}) \subseteq [H_f]$, $\forall \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$. The interval Hessian matrix family $[H_f]$ is then used to formulate a theorem in which the α calculation problem is relaxed.

Theorem 2.2.2 *Consider a general function $f(\boldsymbol{x})$ with continuous second-order derivatives and its Hessian matrix $H_f(\boldsymbol{x})$. Let $\mathcal{L}(\boldsymbol{x})$ be defined by Equation (8). Let $[H_f]$ be a real symmetric interval matrix such that $H_f(\boldsymbol{x}) \subseteq [H_f]$, $\forall \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$. If the matrix $[H_{\mathcal{L}}]$ defined by $[H_{\mathcal{L}}] = [H_f] + 2\,\Delta = [H_f] + 2\,\mathrm{diag}\,(\alpha_i)$ is positive semi-definite, then $\mathcal{L}(\boldsymbol{x})$ is convex over the domain $[\boldsymbol{x}^L, \boldsymbol{x}^U]$.*

One of the most effective procedures for the rigorous calculation of the α parameters is via the following Scaled Gerschgorin Theorem (Adjiman *et al.* (1998a)).

Theorem 2.2.3 *For any vector $\boldsymbol{d} > 0$ and a symmetric interval matrix $[A]$, define the vector α as*

$$\alpha_i = \max \left\{ 0, -\frac{1}{2} \left(\underline{a}_{ii} - \sum_{j \neq i} |a|_{ij} \frac{d_j}{d_i} \right) \right\}$$

where $|a|_{ij} = \max\{|\underline{a}_{ij}|, |\overline{a}_{ij}|\}$.

Then, for all $A \in [A]$, the matrix $A_{\mathcal{L}} = A + 2\Delta$ with $\Delta = \mathrm{diag}(\alpha_i)$ is positive semi-definite.

Overall Valid Convex Underestimator A function $f(\boldsymbol{x})$ with continuous second-order derivatives can be written as

$$\begin{array}{rl} f(\boldsymbol{x}) & = LT(\boldsymbol{x}) + CT(\boldsymbol{x}) + \sum_{i=1}^{bt} b_i x_{B_i,1} x_{B_i,2} \\ & + \sum_{i=1}^{ft} f_i \frac{x_{F_i,1}}{x_{F_i,2}} + \sum_{i=1}^{ut} UT_i(x^i) + \sum_{i=1}^{nt} NT_i(\boldsymbol{x}) \end{array}$$

where $LT(\boldsymbol{x})$ is a linear term; $CT(\boldsymbol{x})$ is a convex term; bt is the number of bilinear terms, $x_{B_i,1}$ and $x_{B_i,2}$ denote the two variables that participate in the ith bilinear term and b_i is its coefficient; ft is the number of fractional terms, $x_{F_i,1}$ and $x_{F_i,2}$ denote the two variables that participate in the ith fractional term and f_i is its coefficient; ut is the number of univariate concave terms, $UT_i(x^i)$ is the ith univariate concave term, x^i denotes the variable that participates in UT_i; nt is the number of general nonconvex terms, $NT_i(\boldsymbol{x})$ is the ith general nonconvex term.
The corresponding convex lower bounding function is

$$\begin{array}{l} \mathcal{L}(\boldsymbol{x}, \boldsymbol{w}) = LT(\boldsymbol{x}) + CT(\boldsymbol{x}) \\ + \sum_{i=1}^{bt} b_i w_{B_i} + \sum_{i=1}^{ft} f_i w_{F_i} \\ + \sum_{i=1}^{ut} \left(UT_i(x^{i,L}) + \frac{UT_i(x^{i,U}) - UT_i(x^{i,L})}{x^{i,U} - x^{i,L}} (x - x^{i,L}) \right) \\ + \sum_{i=1}^{nt} \left(NT_i(\boldsymbol{x}) + \sum_{j=1}^{n} \alpha_{ij} (x_j^L - x_j)(x_j^U - x_j) \right) \end{array} \tag{10}$$

where α_{ij} corresponds to term i and variable j and satisfies Theorem 2.2.1. The w_{B_i} variables are defined by Equations (5). The w_{F_i} variables must satisfy constraints of the forms given by (6).

2.3 Procedure for Enclosing All Solutions

The multiple ϵ–global minima of (3), (if any) can then be localized based on a branch and bound procedure involving the successive refinement of convex relaxations (4) of the initial problem (3). Formulation (4) will always underestimate the global minimum of (3) within the same box constraints. Therefore, if the solution of (4) inside some rectangular region is strictly positive, then the solution of (3) inside the same rectangular domain will also be strictly positive. A strictly positive solution for (3) implies that the slack variable s cannot be driven to zero, and thus (1) is guaranteed not to have any solutions inside the rectangular region at hand. This provides a mechanism for fathoming (eliminating) parts of the target region which are guaranteed not to contain any solutions. If on the other hand, the global minimum of (4) is negative then (3) may or may not involve a solution with a zero slack variable and therefore no deduction can be drawn regarding the existence or not of solutions for (1) inside the current rectangular domain. In this case, further partitioning of the current rectangular region is required until the global minimum of (4) becomes positive or a feasible point for (3) is found.

Based on Property 2.3 which demands that the convex lower bounding functions $\hat{h}^{nonc}_{+,j}, \hat{h}^{nonc}_{-,j}, \hat{g}^{nonc}_{k}$ must be tight, the maximum separation between the original functions and the convex underestimators can become arbitrarily ϵ–small by appropriately reducing the size of the rectangular domain. This implies that as the current box constraints $[\boldsymbol{x}^L, \boldsymbol{x}^U]$ collapse into a point the maximum difference ϵ between the original constraint set and its convex relaxation goes to zero. Therefore, any feasible point of problem (4) becomes at least ϵ–feasible for problem (3) by sufficiently tightening the bounds around this point. Tighter box constraints can be realized by partitioning the current rectangular domain into a number of smaller ones.

One way of partitioning is to successively divide the current rectangle into two subrectangles by halving on the middle point of the longest side of the initial rectangle (bisection). At each iteration the lower bound of (3) is simply the infimum over all the minima of problem (4) in every subrectangle composing the initial rectangle. Therefore, a straightforward (bound improving) way of tightening the lower bound is to halve at each iteration, only the subrectangle responsible for the infimum of the minima of (4) over all subrectangles, according to the rules discussed earlier. If the global minimum of (4) in any subrectangle is strictly greater than zero, then we can safely ignore this subrectangle (fathoming step) because the global minimum of (3) cannot be situated inside it. This procedure generates a *nondecreasing* sequence for the lower bound of (3) yielding a set of candidate rectangles for containing a solution of (1). Convergence is reached when none of the rectangles involve a negative lower bound (no solutions), or when all of the remaining rectangles with negative lower bounds are within the prespecified size tolerance ϵ_r. A detailed algorithmic description can be found in Maranas and Floudas (1995) and in the forthcoming book by Floudas (2000).

Remark 2.2 Even if the number of multiple global minima of (3) is finite Hansen *et al.* (1992b) have shown that no algorithm can locate all of them with a finite number of function evaluations. Furthermore, a corrolary of this result (Hansen *et al.*, 1992b) is that no algorithm can always localize, with a finite number of function evaluations, all globally optimal points by compact subintervals in one–to–one correspondence with them. Therefore, a more reasonable aim than finding all global minima of (3) is to find arbitrarily small disjoint subintervals containing all globally optimal points of (3) if any.

2.4 Computational Studies

In this section, two classes of problems are addressed to illustrate the applicability and efficiency of the deterministic global optimization approach for the enclosure of all solutions of nonlinear constrained systems of equations.

2.4.1 Multiple Steady States

This example, presented in detail by Kubicek *et al.* (1980), is a model of two continuous, non–adiabatic, stirred tank reactors in series at steady state with recycle and an exothermic, first order, irreversible reaction. After elimination of certain variables, the mathematical model yields the following system of equations in two variables ϕ_1, ϕ_2 that represent the dimensionless temperatures in the reactors:

$$\begin{gathered}(1-R)\left[\tfrac{D}{10(1+\beta_1)}-\phi_1\right]\exp\left(\tfrac{10\phi_1}{1+10\phi_1/\gamma}\right)-\phi_1=0\\ (1-R)\left[D/10-\beta_1\phi_1-(1+\beta_2)\phi_2\right]\exp\left(\tfrac{10\phi_2}{1+10\phi_2/\gamma}\right)\\ +\phi_1-(1+\beta_2)\,\phi_2=0\end{gathered} \tag{11}$$

$$0 \;\le\; \phi_i \;\le\; 1, \;\; i=1,2.$$

Note that the nonlinear terms,

$$\exp\left(\frac{10\phi_i}{1+10\phi_i/\gamma}\right), \;\; \phi_i \exp\left(\frac{10\phi_i}{1+10\phi_i/\gamma}\right), \;\; i=1,2$$

appearing in this system are convex and thus are left unchanged in the lower bounding problem. The negative of these terms are concave functions and are convex lower bounded with a line segment. The terms,

$$\pm\phi_1 \exp\left(\frac{10\phi_2}{1+10\phi_2/\gamma}\right),$$

are products of two univariate functions and are underestimated based on the analysis of Maranas and Floudas (1995).

The problem was solved for different values of the recycle ratio R, starting with R=0.935 and ending at R=0.995 with 0.005 increments. For each value of R, the total number of distinct solutions, the total number of iterations and CPU requirements are shown in Table 1 for both the GAMS and the αBB implementation.

2.4.2 All Homogeneous Azeotropes

The ability to predict whether a given mixture will form one or more homogeneous, heterogeneous and reactive azeotropes and to calculate the conditions and compositions of each azeotrope is essential in modeling separation processes.

Considering here the case of homogeneous azeotropes (i.e., one liquid phase), there are three thermodynamic conditions which a system must meet in order for an homogeneous azeotrope to exist. These conditions are: (i) equilibrium, (ii) the composition of vapor phase must be identical to the overall composition of the liquid phase, and (iii) the mole fractions of the components in each phase must sum to unity and must be non-negative.

The equilibrium condition requires that the chemical potential of each component must be the same in all phases. Since an homogeneous azeotropic system contains a vapor phase (V), and only one liquid phase (L), this condition can be written:

$$\mu_i^V = \mu_i^L \qquad \forall\, i \in N \tag{12}$$

where μ_i^V and μ_i^L represent the chemical potential of component i in the vapor and liquid phases. From the definition of the fugacity of component i in a mixture, $\hat{f}_i$,

$$\hat{f}_i^V = \hat{f}_i^L \qquad \forall\, i \in N \tag{13}$$

hence,

$$y_i \hat{\phi}_i^V P = x_i \gamma_i^L f_i^L. \tag{14}$$

The symbol $\hat{\phi}_i^V$ represents the mixture fugacity coefficient of component i in the vapor phase. For the liquid phase, γ_i^L is the activity coefficient, and f_i^L is the fugacity of component i in the liquid phase. Assuming that the vapor phase can be modeled as an ideal gas, we have :

$$\frac{y_i}{x_i} = \frac{\gamma_i^L P_i^{sat}}{P}. \tag{15}$$

Note that all of the nonidealities of the system are confined to the activity coefficient term. For instance, employing the Wilson activity coefficient (Wilson, 1964) equation we have :

$$\ln \gamma_i = 1 - \ln\left(\sum_{j\in N} x_j \Lambda_{ij}\right) - \sum_{j \in N} \frac{x_j \Lambda_{ji}}{\sum\limits_{k\in N} x_k \Lambda_{jk}} \tag{16}$$

where Λ_{ij} is the nonsymmetric binary interaction parameter between components i and j with $\Lambda_{ii} = 1$.

The saturated vapor pressure is calculated using the Antoine equation:

$$\ln P_i^{sat} = a_i - \frac{b_i}{T + c_i} \tag{17}$$

where a_i, b_i, and c_i are constant parameters with a_i and b_i being positive, while c_i may be positive or negative but $| c_i | < T$.
Condition (ii) takes the form:

$$y_i = x_i \qquad \forall\, i \in N. \tag{18}$$

Condition (iii) requires that the mole fractions in each phase sum to unity and have values between 0 and 1.

$$\begin{gathered} \sum_{i\in N} y_i = \sum_{i \in N} x_i = 1 \\ 0 \le y_i, x_i \le 1 \qquad \forall\, i \in N. \end{gathered} \tag{19}$$

This mathematical model corresponds to a nonlinear constrained system of equations that exhibits multiplicity of solutions and each solution is an homogeneous azeotrope.

Acetone/Methyl Acetate/Methanol : A common system encountered often in the literature of phase equilibria problems is the Acetone/Methyl Acetate/Methanol system, (Fidkowski *et al.* (1993)). The Wilson equation and the NRTL equation are used to model the liquid phase activity coefficients. As can be seen in Table 2, the Wilson equation predicted all four azeotropes. The Acetone-Methanol and Methyl Acetate-Methanol binary azeotrope predictions are close to the experimental results. On the other hand, the prediction for the Acetone-Methyl Acetate azeotrope and the ternary azeotrope are significantly different than the experimental results. In general, the NRTL equation gave better results for the prediction of the binary azeotropes, but the NRTL equation does not predict a ternary azeotrope.

The computational requirements for calculating the binary azeotropes were under one cpu second for both activity coefficient models. In Table 2, the column *NLP Subs.* refers to the number of nonlinear subproblems that were solved in order to converge to the global solution. For the binary systems in this example, about forty nonlinear subproblems were solved per CPU second. In the ternary system, about thirty subproblems were solved per CPU second, due to the larger size of the problem. For the ternary azeotrope with the Wilson model, the cpu requirement was 7.39 seconds.

Conclusions

This review paper presented the recent advances in global optimization for process synthesis, design and control. The focal point was on novel deterministic global optimization methods for the enclosure of all solutions of nonlinear constrained systems of equations.

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R	Iter-GAMS	CPU-GAMS	Iter-αBB	CPU-αBB	# Sol's
0.935	65	3.78	52	2.7	1
0.940	82	4.71	51	2.7	1
0.945	437	18.84	117	5.5	3
0.950	340	15.72	161	6.9	5
0.955	317	14.79	162	6.6	5
0.960	539	25.11	216	8.6	7
0.965	267	12.57	156	6.3	5
0.970	270	13.02	154	6.1	5
0.975	214	10.62	155	6.3	5
0.980	240	11.07	149	6.1	5
0.985	228	11.57	141	11.6	5
0.990	65	3.55	60	3.6	1
0.995	23	1.26	41	1.3	1

Table 1: Number of solutions, iterations, and CPU requirements for different recycle ratios

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Results for Acetone (1) – Methyl Acetate (2) – Methanol (3) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)	NLPs
Wilson Equation						
1-2	0.532	0.468	—	55.675	0.47	21
1-3	0.747	—	0.253	54.505	0.37	17
2-3	—	0.677	0.323	54.356	0.43	17
1-2-3	0.272	0.465	0.253	54.254	7.39	217
NRTL Equation						
1-2	0.655	0.345	—	55.557	0.94	29
1-3	0.777	—	0.223	55.117	0.57	19
2-3	—	0.663	0.337	53.545	0.52	19
1-2-3	No ternary azeotrope was found using the NRTL Equation					

Table 2: N-ary Solutions for Example