GLOBAL OPTIMIZATION IN DESIGN AND CONTROL OF CHEMICAL PROCESS SYSTEMS

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Abstract: This paper presents an overview of the recent advances in deterministic global optimization approaches and their applications in the areas of Process Design and Control. The focus is on global optimization methods for (a) twice-differentiable constrained nonlinear optimization problems, (b) mixed-integer nonlinear optimization problems, and (c) locating all solutions of nonlinear systems of equations. Theoretical advances and computational studies on process design, batch design under uncertainty, phase equilibrium, location of azeotropes, stability margin, process synthesis, and parameter estimation problems are discussed.

Keywords: Global Optimization; Twice Differentiable NLPs; Mixed-Integer Nonlinear Optimization; Locating All Solutions; αBB approach, Design and Control

1. INTRODUCTION

A significant effort has been expended in the last five decades toward theoretical and algorithmic studies of applications that arise in Process Design and Control. In the last decade we have experienced significant interest in Chemical Engineering for new methods of global optimization as well as the application of available global optimization algorithms to important engineering problems.

The existing approaches for global optimization are classified as deterministic or probabilistic. The deterministic approaches include: (a) Lipschitzian methods, (b) Branch and Bound methods, (c) Cutting Plane methods, (d) Difference of Convex (D.C.) and Reverse Convex methods, (e) Outer Approximation methods, (f) Primal-Dual methods, (g) Reformulation-Linearization methods, and (h) Interval methods. The probabilistic methods include (i) random search approaches, and (ii) clustering methods. Recent books that discuss the above classes are available by Pardalos and Rosen (1987), Torn and Zilinskas (1989), Ratschek and Rokne (1988), Horst and Tuy (1990), Neumaier (1990), Floudas and Pardalos (1992), Horst and Pardalos (1995), Horst et al. (1995), Pinter (1996), Grossmann (1996) and Floudas and Pardalos (1996).

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 (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

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a series of reverse convex problems, and Tsirukis and Reklaitis (1993 a,b) proposed a feature extraction algorithm for constrained global optimization. Maranas and Floudas (1992, 1993, 1994a,b) 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. This result is very significant because it extends the classes of mathematical problems that the GOP can be applied to nonlinear objective function and constraints that are twice-continuously differentiable. Vaidyanathan and El-Halwagi (1994) proposed an interval analysis based global optimization method and Ryoo and Sahinidis (1995) suggested the application of reduction tests within the framework of branch and bound methods. 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. 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. In a series of papers McDonald and Floudas (1994;1995a,b,c) 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 activity coefficient models. McDonald and Floudas (1997) proposed the combination of the two aforementioned classes of problems, developed a special purpose program GLOPEQ, and performed an extensive computational study on difficult phase equilibrium problems. Hua et al. (1996) applied an interval analysis method for the phase stability computations of binary and ternary mixtures. The books of Floudas and Pardalos (1996) and Grossmann (1996) contain a number of recent chemical engineering contributions (not presented here due to space limitations), and the review paper of Floudas (1997) presents an overview of these recent chemical engineering contributions and the advances in global optimization based on the decomposition approach GOP, the generalized geometric programming, and the αBB approach. 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. 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. 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.

Adjiman and Floudas (1996) proposed novel approaches for the rigorous determination of the α parameters that are employed in the αBB global optimization approach. These methods are based on a modified Kharitonov theorem for interval polynomials, interval anlysis of the hessian matrices and calculate rigorous bounds on the minimum eigenvalue for general twice differentiable problems. Furthermore, 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.

In this paper, we will focus on our recently proposed deterministic global optimization method denoted as αBB, and present the key contributions in addressing (a) twice-differentiable NLPs, (b) mixed-integer nonlinear problems, and (c) the location of all solutions of nonlinear systems of equations.

2. THE αBB APPROACH FOR GENERAL NLPS

The αBB algorithm is based on a branch-and-bound framework and addresses nonconvex minimization problems of the formulation (1). The theoretical properties of the algorithm guarantee that such a problem can be solved to global optimality with finite ϵ-convergence.

$$
\begin{array}{rl}
\min\limits_{\boldsymbol{x}} & f(\boldsymbol{x}) \\
s.t. & \boldsymbol{g}(\boldsymbol{x}) \leq 0 \\
& \boldsymbol{h}(\boldsymbol{x}) = 0 \\
& \boldsymbol{x} \in X \subseteq \Re^n
\end{array}
\tag{1}
$$

where f, $\boldsymbol{g}$ and $\boldsymbol{h}$ belong to $\mathcal{C}^2$, the set of twice-differentiable functions, and $\boldsymbol{x}$ is an n-vector.

Each iteration of the algorithm consists of a *branching* step and a *bounding* step. In the *branching step*, a lower bound is obtained by constructing valid convex underestimators for the functions in the problem and solving the resulting convex NLP to global optimality. An upper bound is calculated either by solving the original problem locally over each subdomain of the solution space or by performing a problem evaluation at the solution of the lower bounding problem. The identification of the global optimal solution depends on the validity of the lower bounding problems as well as the construction of increasingly tight lower bounding problems for successive partitions of the solution space. Such properties lead to the generation of a *nondecreasing sequence* of lower bounds which progresses towards the optimal solution.

An 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) and Adjiman et al. (1998a,b).

Bilinear Terms : In the case of a bilinear term xy, 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 :

$$
\begin{array}{l}
w_B \geq x^L y + y^L x - x^L y^L, \\
w_B \geq x^U y + y^U x - x^U y^U.
\end{array}
\tag{2}
$$

An upper bound can be imposed on w to construct a better approximation of the original problem (McCormick, 1976). This is achieved through the addition of two linear constraints:

$$
\begin{array}{l}
w_B \leq x^U y + y^L x - x^U y^L, \\
w_B \leq x^L y + y^U x - x^L y^U.
\end{array}
\tag{3}
$$

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.

$$
\begin{array}{l}
w_F \geq \begin{cases} x^L/y + x/y^U - x^L/y^U & \text{if } x^L \geq 0 \\ x/y^U - x^L y/y^L y^U + x^L/y^L & \text{if } x^L < 0 \end{cases} \\
w_F \geq \begin{cases} x^U/y + x/y^L - x^U/y^L & \text{if } x^U \geq 0 \\ x/y^L - x^U y/y^L y^U + x^U/y^U & \text{if } x^U < 0 \end{cases}
\end{array}
\tag{4}
$$

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:

$$
ut(x^L) + \frac{ut(x^U) - ut(x^L)}{x^U - x^L}(x - x^L). \tag{5}
$$

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

$$
\mathcal{L}(\boldsymbol{x}) = f(\boldsymbol{x}) + \sum_{i=1}^{n} \alpha_i (x_i^L - x_i)(x_i^U - x_i) \tag{6}
$$

where the α_i's are positive scalars.

Since the summation term in Equation (6) 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*. Since $\mathcal{L}(\boldsymbol{x})$ is convex if and only if its Hessian matrix $H_{\mathcal{L}}(\boldsymbol{x})$ is positive semi-definite, 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

$$
H_{\mathcal{L}}(\boldsymbol{x}) = H_f(\boldsymbol{x}) + 2\,\Delta, \tag{7}
$$

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 (6), 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 2.0.1. $\mathcal{L}(\boldsymbol{x})$, as defined in Equation (6), 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).

2.1 *Overall Valid Convex Underestimator*

Based on the underestimators discussed for each of the term types identified, a convex underestimator for any given twice-differentiable function can now be obtained through a decomposition approach. A function $f(\boldsymbol{x})$ with continuous second-order derivatives can be written as

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

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 lower bounding function is

$$\begin{aligned}
&\mathcal{L}(\boldsymbol{x},\boldsymbol{w}) = LT(\boldsymbol{x}) + CT(\boldsymbol{x}) \\
&+ \sum_{i=1}^{bt} b_i w_{B_i} + \sum_{i=1}^{ft} f_i w_{F_i} \\
&+ \sum_{i=1}^{ut} \left(UT_i(x^{i,L}) + \frac{UT_i(x^{i,U}) - UT_i(x^{i,L})}{x^{i,U} - x^{i,L}} (x - x^{i,L}) \right) \\
&+ \sum_{i=1}^{nt} \left(NT_i(\boldsymbol{x}) + \sum_{j=1}^{n} \alpha_{ij} (x_j^L - x_j)(x_j^U - x_j) \right)
\end{aligned} \tag{8}$$

where α_{ij} corresponds to term i and variable j and satisfies Theorem 2.0.1. The w_{B_i} variables are defined by Equations (2) and (3). The w_{F_i} variables must satisfy constraints of the forms given by (4).

If the nonlinear equality constraints contain convex or general nonconvex terms, the equalities obtained by simple substitution of the corresponding underestimators are nonlinear. In the presence of convex, general nonconvex or univariate concave terms, the original equalities $h(\boldsymbol{x}) = 0$ must therefore be rewritten as two inequalities of opposite signs, and these two inequalities must then be underestimated independently. The univariate concave terms appearing in the nonconvex equality become convex in one of the two inequalities while the convex terms become concave and the general nonconvex terms become convex or remain nonconvex. A detailed description of handling the equalities is in Adjiman et al. (1998a,b).

3. RIGOROUS CALCULATION OF α FOR GENERAL NLPS

The focus of this section is the development of methods that generate rigorously a set of α parameters satisfying Theorem 2.0.1. This allows the construction of a convex underestimator $\mathcal{L}(\boldsymbol{x})$ for a twice-differentiable function $f(\boldsymbol{x})$ over a specified domain. Two classes of approaches to this problem are defined as: (i) uniform diagonal shift of the Hessian matrix of $f(\boldsymbol{x})$, and (ii) non-uniform diagonal shift of the Hessian matrix of $f(\boldsymbol{x})$.

As seen in Equation (7) and Theorem 2.0.1, the diagonal shift matrix Δ is closely linked to the Hessian matrix $H_f(\boldsymbol{x})$ of the function being underestimated. For general twice-differentiable functions, the elements of the Hessian matrix $H_f(\boldsymbol{x})$ are likely to be nonlinear functions of the variables. The difficulty arising from the presence of the variables in the convexity condition can be overcome through the transformation of the exact $\boldsymbol{x}$-dependent Hessian matrix to an interval matrix $[H_f]$ such that $H_f(\boldsymbol{x}) \subseteq [H_f]$, $\forall \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U]$. The elements of the original Hessian matrix are treated as independent when calculating their natural interval extensions (Neumaier, 1990). The interval Hessian matrix family $[H_f]$ is then used to formulate a theorem in which the α calculation problem is relaxed.

Theorem 3.0.1. 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 (6). 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 $[\boldsymbol{x}^L, \boldsymbol{x}^U]$.

The quality of the underestimator generated by any given α calculation method can be measured in terms of the separation distance between the nonconvex function and its underestimator: the tighter the lower bounding scheme, the faster the convergence. For this purpose, the maximum separation distance between $f(\boldsymbol{x})$ and $\mathcal{L}(\boldsymbol{x})$, d_{max}, can be used. Maranas and Floudas (1994) showed that it is directly proportional to the α_i's and given by

$$d_{max} = \frac{1}{4} \sum_{i=1}^{n} \alpha_i (\boldsymbol{x}_i^U - \boldsymbol{x}_i^L)^2 \tag{9}$$

In addition, the α parameters and the bounds on the variables can be shown to affect the maximum number of iterations required in order to achieve ϵ-convergence (Maranas and Floudas, 1994).

In the sequel, two rigorous methods for the calculation of the α parameters are outlined. These methods are based on the non-uniform diagonal shift matrix and the details of their proofs as well as several other methods are in Adjiman et al. (1998a).

Method 1: Scaled Gerschgorin Theorem

Theorem 3.0.2. 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.

Method 2: Minimization of Maximum Separation Distance

Since the maximum separation distance between the original function and its underestimator reflects the quality of the underestimator, this method aims at deriving a non-uniform diagonal shift matrix Δ which is optimal with respect to d_{max}. This goal can be expressed as an optimization problem of the form

$$\begin{aligned} &\min\ (\boldsymbol{x}^U - \boldsymbol{x}^L)^T\Delta(\boldsymbol{x}^U - \boldsymbol{x}^L) \\ &s.t.\ \ H_f(\boldsymbol{x}) + 2\Delta \geq 0 \\ &\qquad \boldsymbol{x} \in [\boldsymbol{x}^L, \boldsymbol{x}^U] \end{aligned}$$

where Δ is a diagonal matrix, and $M \geq 0$ means that the matrix M is positive semi-definite.

Due to the nonconvexity of the above problem, the formulation is relaxed to

$$\begin{aligned} &\min\ (\boldsymbol{x}^U - \boldsymbol{x}^L)^T\Delta(\boldsymbol{x}^U - \boldsymbol{x}^L) \\ &s.t.\ \ [H_f] + 2\Delta \geq 0 \end{aligned}$$

The presence of the interval Hessian matrix in the constraint makes the identification of the solution of this problem difficult. To further simplify it, $[H_f]$ can be replaced by a real matrix whose minimum eigenvalue is smaller than the minimum eigenvalue of $[H_f]$. The lower bounding Hessian L is a natural choice and the maximum distance minimization problem becomes (see Adjiman et al. 1998a):

$$\begin{aligned} &\min\ (\boldsymbol{x}^U - \boldsymbol{x}^L)^T\Delta(\boldsymbol{x}^U - \boldsymbol{x}^L) \\ &s.t.\ \ L + 2\Delta \geq 0 \end{aligned} \tag{10}$$

Problem (10), a semi-definite programming problem, is convex and can therefore be solved to global optimality using interior-point methods which have a polynomial worst-case complexity.

4. MIXED-INTEGER NONLINEAR OPTIMIZATION

A wide range of chemical engineering problems can effectively be framed as *Mixed–Integer Nonlinear Problems* (MINLP) as this approach allows the simultaneous optimization of the continuous variables pertaining to a certain structure, and of the structure itself which is modeled via binary variables (Floudas, 1995; Grossmann 1990,1996a). Such a mathematical framework has been proposed for a variety of process synthesis problems (e.g., heat recovery networks, separation systems, reactor networks), process operations problems (e.g., scheduling and design of batch processes), molecular design problems and synthesis of metabolic pathways. A number of these applications are described in Floudas (1995) and Grossmann (1996a). The degree of nonconvexity of the participating functions is generally arbitrary and nonlinearities can be identified in the continuous, the integer, or joint domains. The difficulties in solving these MINLPs therefore stem not only from the combinatorial characteristics of the problem which are a direct result of the presence of the integer variables, but also from the presence of nonconvexities (Floudas and Grossmann, 1995).

4.1 *The SMIN–αBB Algorithm*

The SMIN–αBB algorithm is a global optimization algorithm for MINLPs of the form :

$$\begin{aligned} \min_{\boldsymbol{x}}\ & f(\boldsymbol{x}) + \boldsymbol{x}^T A_0 \boldsymbol{y} + c_0^T \boldsymbol{y} \\ s.t.\ & \boldsymbol{g}(\boldsymbol{x}) + \boldsymbol{x}^T A_1 \boldsymbol{y} + c_1^T \boldsymbol{y} \leq 0 \\ & \boldsymbol{h}(\boldsymbol{x}) + \boldsymbol{x}^T A_2 \boldsymbol{y} + c_2^T \boldsymbol{y} = 0 \\ & \boldsymbol{x} \in X \subseteq \Re^n \\ & \boldsymbol{y} \in Y = \{0,1\}^m \end{aligned} \tag{11}$$

where f, $\boldsymbol{g}$ and $\boldsymbol{h}$ belong to $\mathcal{C}^2$, the set of functions with continuous second–order derivatives, $\boldsymbol{x}$ is a vector of size n, $\boldsymbol{y}$ is a vector of size m, A_0, A_1, A_2 are $n \times m$ real matrices and c_0, c_1, c_2 are real vectors of size m.

As can be seen from (11), the binary variables can participate linearly or in bilinear mixed integer terms. Although this condition may appear restrictive at first, many other types of integer or mixed–integer terms can be transformed into this form through the introduction of additional variables.

The global optimum of a problem of type (11) is identified using a branch–and–bound scheme which allows the generation of converging sequences of valid upper and lower bounds. The branch–and–bound tree is constructed by branching on a combination of the continuous and binary variables. For each region of the solution space thus obtained, a convex lower bounding MINLP is derived and solved to global optimality using the OA algorithm, the GBD algorithm or the linear underestimators of Glover (see Floudas, 1995), depending on the type of participation of the binary variables. If this problem is infeasible, or if its solution is greater than the current upper bound for problem (11), the region is fathomed. Otherwise, an upper bound is generated through the solution of the original nonconvex MINLP restricted to the current domain. The results are then used to guide further exploration of the solution space : the node with the smallest lower bound is split into two new domains. Combined with an underestimating strategy which provides gradually tighter convex lower bounding problems, this approach results in the identification of the global optimum solution with ϵ–convergence.

4.2 *The GMIN–αBB Algorithm*

The GMIN–αBB algorithm is a global optimization algorithm for general MINLPs of the form :

$$\begin{aligned} \min_{\boldsymbol{x},\boldsymbol{y}} \quad & f(\boldsymbol{x},\boldsymbol{y}) \\ s.t. \quad & \boldsymbol{g}(\boldsymbol{x},\boldsymbol{y}) \leq 0 \\ & \boldsymbol{h}(\boldsymbol{x},\boldsymbol{y}) = 0 \\ & \boldsymbol{x} \in X \subseteq \Re^n \\ & \boldsymbol{y} \in Y = \{0,1\}^m \end{aligned} \tag{12}$$

where f, $\boldsymbol{g}$ and $\boldsymbol{h}$ belong to $\mathcal{C}^2$, the set of twice-differentiable functions, $\boldsymbol{x}$ is a vector of size n, $\boldsymbol{y}$ is a vector of size m.

As seen from the formulation, arbitrary twice–continuous non–convex terms in which both continuous and binary variables participate are allowed. Thus, the proposed framework addresses a very general class of MINLP problems.

The key idea of the GMIN–αBB algorithm is to embed the αBB algorithm within a branch and bound framework which handles the binary variables. At each node of the branch and bound tree a continuous relaxation of the original problem is being solved, with some of the binary variables fixed to 0 or 1, according to the branching rules that are discussed in a subsequent section. The most important consequence of this approach is that the continuous relaxation at each node is a *non–convex* NLP whose *global optimum solution* can provide a guaranteed lower bound to the MINLP problem. It is therefore crucial to be able to solve each branch and bound node efficiently to global optimality. Note that any lower bound on the global solution of these non–convex NLPs is a valid lower bound for the global solution of the original MINLP problem. The αBB algorithm is employed so as to provide valid lower bounds for the outer branch and bound algorithm. A detailed description of the three major components of the GMIN–αBB approach, namely the lower bound generation, the selection of branching variables, and the selection of branching nodes can be found in Adjiman et al. (1997).

5. LOCATING ALL SOLUTIONS OF NONLINEAR SYSTEMS OF EQUATIONS

A fundamental task in many chemical engineering problems is finding all solutions of a set of equations. Typical examples of such tasks in chemical engineering include (i) the well known identification of potential multiplicities of exothermic reactions occurring in adiabatic CSTR's; (ii) 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) identification of multiple solutions for porous catalysts effectiveness factors in exothermic reactions ; (v) solution of (un)constrained simulation problems in steady–state flowsheet modelling; (vi) identification of equilibrium points in (un)reacting multiphase systems such as multiple miscibility gaps in liquid–liquid equilibria; (vii) prediction of all homogeneous/heterogeneous azeotropes or eutectic points at some temperature or pressure for given activity models; and (viii) location of all multiple steady states of individual distillation columns as well as of interlinked separation systems.

Maranas and Floudas (1995) proposed a new approach for finding all ϵ–feasible solutions for certain classes of nonlinearly constrained systems of equations. This is formulated as:

$$\begin{aligned} h_j(\boldsymbol{x}) = 0, \quad & j \in \mathcal{N}_E \\ g_k(\boldsymbol{x}) \leq 0, \quad & k \in \mathcal{N}_I \\ \boldsymbol{x}^L \leq \boldsymbol{x} \leq & \boldsymbol{x}^U, \end{aligned} \tag{13}$$

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

By introducing a single slack variable s, formulation (13) can be written as :

$$\begin{aligned} \min_{\boldsymbol{x},s \geq 0} \quad & s \\ \text{subject to} \quad & h_j(\boldsymbol{x}) - s \leq 0, \quad j \in \mathcal{N}_E \\ & -h_j(\boldsymbol{x}) + s \leq 0, \quad j \in \mathcal{N}_E \\ & g_k(\boldsymbol{x}) \leq 0, \quad k \in \mathcal{N}_I \\ & \boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U. \end{aligned} \tag{14}$$

There is a one to one correspondence between multiple global minima $(\boldsymbol{x}^*, s^*)$ of (13) for which $s^* = 0$ and solutions of (14). This means that if the global minimum of (13) involves a nonzero slack variable s^* then the original problem (14) has no solutions.

However, even if the number of multiple global minima of (13) is finite it has been shown that no algorithm can locate all of them with a finite number of function evaluations. A corrolary of this result 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 is to find arbitrarily small disjoint subintervals containing all globally optimal points of (14) if any.

These multiple ϵ–global minima of (14), (if any) can then be localized based on a branch and bound procedure involving the successive refinement of convex relaxations *(R)* of the initial problem. Formulation *(R)* is obtained by replacing the nonconvex functions with some *tight, convex lower bounding* functions by following the techniques discussed in section 2. Because *(R)* is convex its global minimum within some box constraints can be routinely found and will always underestimate the global minimum of (14) within the same box constraints. A strictly positive solution for (14) implies that the slack variable s cannot be driven to zero, and thus (13) 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 *(R)* is negative then (14) 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 (13) inside the current rectangular domain. In this case, further partitioning of the current rectangular region is required until the global minimum of *(R)* becomes positive (fathoming) or a feasible point for (14) is found (convergence). The branch and bound procedure of Maranas and Floudas (1995) generates a *nondecreasing* sequence for the lower bound of (14) yielding a set of candidate rectangles for containing a solution of (13). 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.

6. COMPUTATIONAL STUDIES

Extensive computational studies on important problems in chemical process design and control have been contacted for all the theoretical and algorithmic advances presented in sections 2, 3, 4, and 5. More specifically, the αBB global optimization approach for twice differentiable constrained NLPs has been applied to blending and pooling problems, to linearly constrained concave programming problems, to reactor design, to nonsharp separation synthesis problems, to heat exchanger network design, to robust stability analysis problems, to generalized geometric programming problems. The SMIN–αBB and the GMIN–αBB have been applied to small MINLP literature problems, as well as heat exchanger network synthesis problems, the design of multilevel pump configurations, and a variety of trim loss problems that arise in the paper industry, where small to medium size problems have been addressed effectively. The method for enclosing all solutions of constrained systems of equations has been applied for steady state identification in reaction networks, equilibrium processes, multiple steady states in CSTRs, robot kinematics, and circuit design problems.

Recent important modifications of the αBB approach were introduced by Harding and Floudas (1997) for the batch process design under uncertainty, and by Esposito and Floudas (1998) for the parameter estimation of nonlinear algebraic models using the error in variables approach. In the former approach, it was shown that analytical calculations of the α parameters are indeed possible and this allowed for large scale problems to be addressed to global optimality. These include problems up to 16,000 variables. In the latter approach, the effect of different underestimation alternatives that exploit the mathematical structure along with the role of branching variables and the updates of the bounds are evaluated and it is shown for the first time that that parameter estimation problems can be solved efficiently to global optimality. Additional recent areas where the αBB has been an important component include the nesting and packing of arbitrary objects, the protein folding and peptide docking problems in computational chemistry and biology. Recent key modifications of the approach for locating all solutions have been introduced by Harding et al. (1997) for the determination of all homogeneous azeotropes, while cuurent research work focuses on enclosing all heterogeneous and reactive azeotropes, performing rigorous reactive flash calculations, and locating all transition states in molecular systems.

In the following, we will present an illustrative application in the area of robust stability analysis of control systems.

6.1 *Robust Stability Analysis of Nonlinear Systems*

Robust stability analysis of nonlinear systems involves the identification of the largest possible region in the uncertain model parameter space for which the controller manages to attenuate any disturbances in the system. The stability of a feedback structure is determined by the roots of the closed loop characteristic equation:

$$\det\left(I + P(s,\boldsymbol{q})C(s,\boldsymbol{q})\right) \;=\; 0$$

where $\boldsymbol{q}$ is the vector of the uncertain model parameters, and $P(s), C(s)$ the transfer functions of the plant and controller respectively. The "zero exclusion condition" implies that a system with characteristic equation $P(s,\boldsymbol{q}) = 0$ is stable only if it does not have any roots on the imaginary axis for any realization of the $\boldsymbol{q}$'s in the uncertain model parameter space $\mathcal{Q}$. A stability margin k_m can then be defined as follows:

$$k_m(j\omega) \;=\; \inf\left\{k \;:\; P\left(j\omega,\; \boldsymbol{q}(k)\right) \;=\; 0, \,\forall\, \boldsymbol{q} \;\in\; \mathcal{Q}\right\}$$

Robust stability for this model is then guaranteed if and only if $k_m \;\geq\; 1$.

Checking the stability of a particular system with characteristic equation $P(j\omega, \boldsymbol{q})$ involves the solution of the following nonconvex optimization problem.

$$\min_{q_i, k\geq 0, \omega \geq 0} \quad k \tag{15}$$

$$\begin{aligned} &Re\left[P(j\omega, \boldsymbol{q})\right] = 0 \\ &Im\left[P(j\omega, \boldsymbol{q})\right] = 0 \end{aligned}$$

$$q_i^N - \Delta q_i^-\, k \;\leq\; q_i \leq q_i^N + \Delta q_i^+\, k, \;\; i = 1, \ldots, n$$

where $\boldsymbol{q}^N$ is a stable nominal point for the uncertain parameters and $\Delta\boldsymbol{q}^+, \Delta\boldsymbol{q}^-$ are estimated bounds. Note that it is important to be able to always locate the global minimum of (15), otherwise the stability margin might be overestimated. This overestimation can sometimes lead to the erroneous conclusion that a system is stable when it is not.

Example : This problem was developed to study the stability of the Fiat Dedra spark ignition engine. It involves 9 variables and is highly nonlinear. The stability margin formulation is :

$$\min \;\; k$$

$$\begin{aligned} -a_6(\boldsymbol{q})\omega^6 + a_4(\boldsymbol{q})\omega^4 - a_2(\boldsymbol{q})\omega^2 + a_0(\boldsymbol{q}) = 0 \\ a_7(\boldsymbol{q})\omega^6 - a_5(\boldsymbol{q})\omega^4 + a_3(\boldsymbol{q})\omega^2 - a_1(\boldsymbol{q}) = 0 \end{aligned}$$

$$\begin{aligned} 3.4329 - 1.2721k \leq\; & q_1 \;\leq 3.4329 \\ 0.1627 - 0.06k \leq\; & q_2 \;\leq 0.1627 \\ 0.1139 - 0.0782k \leq\; & q_3 \;\leq 0.1139 \\ 0.2539 \leq\; & q_4 \;\leq 0.2539 + 0.3068k \\ 0.0208 - 0.0108k \leq\; & q_5 \;\leq 0.0208 \\ 2.0247 \leq\; & q_6 \;\leq 2.0247 + 2.4715k \\ 1.0000 \leq\; & q_7 \;\leq 1.0000 + 9.0000k \end{aligned}$$

where

$$a_0(\boldsymbol{q}) = \;\; 6.82079\; 10^{-5} q_1 q_3 q_4^2 + 6.82079\; 10^{-5} q_1 q_2 q_4 q_5$$

$$\begin{aligned} a_1(\boldsymbol{q}) = \;\; & 7.61760\; 10^{-4} q_2^2 q_5^2 + 7.61760\; 10^{-4} q_3^2 q_4^2 \\ & + 4.02141\; 10^{-4} q_1 q_2 q_5^2 + 0.00336706 q_1 q_3 q_4^2 \\ & + 6.82079\; 10^{-5} q_1 q_4 q_5 + 5.16120\; 10^{-4} q_2^2 q_5 q_6 \\ & + 0.00336706 q_1 q_2 q_4 q_5 + 6.82079\; 10^{-5} q_1 q_2 q_4 q_7 \\ & + 6.28987\; 10^{-5} q_1 q_2 q_5 q_6 + 4.02141\; 10^{-4} q_1 q_3 q_4 q_5 \\ & + 6.28987\; 10^{-5} q_1 q_3 q_4 q_6 + 0.00152352 q_2 q_3 q_4 q_5 \\ & + 5.16120\; 10^{-4} q_2 q_3 q_4 q_6 \end{aligned}$$

The remaining nonlinear terms are reported in Adjiman et al. (1998b).

The solution of the stability problem shows that this system is stable and computational results are obtained with $\omega \;\in\; [0, 10]$. Application of the αBB global optimization approach with the Scaled Gerschgorin calculation of the parameters α determines that the system is unstable in 48.9 cpu seconds while the use of the semidefinite programming approach requires 1529 cpu seconds for convergence.

7. CONCLUDING REMARKS

This paper has presented an overview of the advances in the area of deterministic global optimization. This overview focused on global optimization approaches for (a) general twice differentiable NLPs, (b) mixed integer nonlinear optimization problems, and (c) locating all solutions of constrained systems of nonlinear equations. The theoretical advances were outlined along with a summary of the computational studies. An example from the calculation of the stability margin of uncertain control systems illustrated the recent advances.

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