Slovak University of Technology in Bratislava
Institute of Information Engineering, Automation, and Mathematics

PROCEEDINGS

17th International Conference on Process Control 2009

Hotel Baník, Štrbské Pleso, Slovakia, June 9 – 12, 2009

ISBN 978-80-227-3081-5

http://www.kirp.chtf.stuba.sk/pc09

Editors: M. Fikar and M. Kvasnica

Paulen, R., Fikar, M., Čižniar, M., Latifi, M.A.: Global Optimization for Parameter Estimation of Dynamic Systems, Editors: Fikar, M., Kvasnica, M., In *Proceedings of the 17th International Conference on Process Control '09*, Štrbské Pleso, Slovakia, 86–92, 2009.

Full paper online: http://www.kirp.chtf.stuba.sk/pc09/data/abstracts/046.html

GLOBAL OPTIMIZATION FOR PARAMETER ESTIMATION OF DYNAMIC SYSTEMS

R. Paulen [*], **M. Fikar** [*], **M. Čižniar** [*,**], and **M. A. Latifi** [**]

[*] *Slovak University of Technology in Bratislava*
Faculty of Chemical and Food technology
e-mail: {radoslav.paulen, miroslav.fikar, michal.cizniar}@stuba.sk
url: http://www.kirp.chtf.stuba.sk
[**] *Laboratoire des Sciences du Génie Chimique*
CNRS–ENSIC–INPL
1 Rue Grandville, 54001 Nancy Cedex, France
e-mail: latifi@ensic.inpl-nancy.fr

Abstract: This work deals with the problem of finding a global solution for parameter estimation problem of a dynamic system described by a set of ordinary differential equations (ODE). Deterministic spatial branch and bound optimization algorithm is used to find the solution of problem. Upper bound is generated by sequential approach to dynamic optimization problem. Lower bound is provided by a solution of convex relaxation of the original problem. Selected examples from chemical engineering are solved and the resulting solution is discussed.

Keywords: Global Optimization, Convex Relaxation, ODE, Parameter Estimation

1. INTRODUCTION

Human science is now so developed that the optimization problems became the part of daily life of every researcher, developer or designer in engineering, computational chemistry, finance and medicine amongst many other fields. This is especially true if we speak about parameter estimation, when we must find the best possible representation of phenomena (processes) happening in real world, plant or apparatus.

Due to the fact that processes are usually described by set of differential equations, methods of dynamic optimization must be used to find (local) solution of optimization of these processes.

For a number of years, researchers have known that dynamic optimization problems encountered in chemical engineering applications exhibit multiple local optima. This property, which can be attributed to non–convexity of the functions participating in most chemical engineering models, implies that standard local optimization methods will often yield suboptimal solutions to problems. Global optimization algorithms based on the deterministic approach such as generalized Benders decomposition (Geoffrion (1972), Floudas and Visweswaran (1990) and Bagajewicz and Manousiouthakis (1991)), branch and bound (Soland (1971), Ryoo and Sahinidis (1995) and Adjiman et al. (1996)) and interval analysis (Ratschek and Rokne (1988), Vaidyanathan and El-Halwagi (1994) and Han et al. (1997)) guarantee the finite ϵ–convergence (convergence to the global optimum in finite computation steps for a given finite error tolerance) and the global optimality of the obtained solution.

Spatial Branch–and–Bound (sBB) algorithms are the extension of traditional BB algorithms to continuous solution spaces. They are termed "spatial" because they successively partition the Euclidean space where the problem is defined into smaller and smaller regions where the problem is solved

recursively by generating converging sequences of upper and lower bounds to the objective function value. In this work a deterministic sBB global optimization algorithm is used for global dynamic problems with set of first–order parameter dependent differential equations in the constraints, where upper bound is obtained from solution of original dynamic optimization problem using sequential approach. A possible solution with simultaneous approach was described in our previous work (Čižniar et al., 2009). Lower bound is computed by solving the convex relaxed original problem with variable bounding proposed by Papamichail and Adjiman (2004). Strategy of constant bounds is used instead of affine or α–BB bounds (proposed by Papamichail and Adjiman (2002)) due to its usefulness and relative simplicity.

The main purpose of this paper is to demonstrate utilization of sBB global optimization algorithm, to apply successive way to obtain bounds on variables participating on convex relaxation of original problem and to solve chosen examples relevant to chemical engineering.

The paper is organized as follows. Section 2 gives the mathematical formulation of the problem studied. It is a non–convex minimization problem with an initial value problem (IVP) for a set of first–order parameter dependent differential equations in the constraints. Section 3 discusses convex relaxation of original non–convex dynamic optimization problem. Finally in Section 4 selected examples for parameter estimation problems are solved and discussed.

2. PROBLEM STATEMENT

In this section we describe original non–convex dynamic optimization problem. Its solution gives an upper bound for sBB algorithm.

2.1 *Dynamic Process Model*

The processes considered is described by the following set of first–order parameter dependent, typically non–linear, differential equations

$$\dot{x}(t,p) = f\big(t, x(t,p), p\big) \quad \forall t \in \mathcal{I} \equiv [t_0, t_N] \tag{1}$$

where $t \in \mathcal{I} \subset \mathcal{R}$, denotes time as the independent variable and N is the number of points considered additionally to the initial point t_0, $p \subset \mathcal{R}^r$ is the vector of parameters of the process, $x \subset \mathcal{R}^n$ stands for the vector of state variables. The function f is such that $f : \mathcal{I} \times \mathcal{R}^n \times \mathcal{R}^p \to \mathcal{R}^n$. The solution $x(t,p)$ of this set satisfies the initial condition

$$x(t_0, p) = x_0(p) \tag{2}$$

where the function x_0 is such that $x_0 : \mathcal{R}^r \to \mathcal{R}^n$.

2.2 *Process Constraints*

Inequality constraints can be imposed at discrete time points, t_i. These are point constraints of the form

$$g_i\big(x(t_i,p),p\big) \le 0 \qquad i = 0, 1, \ldots, N \tag{3}$$

where the functions $g_i, i = 0, 1, \ldots, N$, are such that $g_i : \mathcal{R}^n \times \mathcal{R}^r \to \mathcal{R}^{s_i}$. Of course any equality point constraint can be replaced by two inequality point constraints. Lower and upper bounds are imposed on the parameters p:

$$p^L \le p \le p^U \tag{4}$$

2.3 *Objective Function*

The objective function for a dynamic optimization problem can be expressed in terms of the values of the state variables at discrete points and of the parameters

$$J\big(x(t_i,p),p;\, i = 0, 1, \ldots, N\big) \tag{5}$$

The function J is such that $J : \mathcal{R}^{n(N+1)} \times \mathcal{R}^r \to \mathcal{R}$. Integral terms that may appear in the objective function can always be eliminated by introducing additional state variables and equations in the set of differential equations.

2.4 *Dynamic Optimization Problem*

The formulation of the dynamic optimization problem studied is given by

$$\begin{aligned} \min_p \; & J\big(x(t_i,p),p;\, i = 0, 1, \ldots, N\big) \\ s.t. \; & \dot{x}(t,p) = f\big(t, x(t,p), p\big) \qquad \forall t \in \mathcal{I} \\ & x(t_0,p) = x_0(p) \\ & g_i\big(x(t_i,p),p\big) \le 0 \qquad i = 0, 1, \ldots, N \\ & p^L \le p \le p^U \end{aligned} \tag{6}$$

The following assumptions are made on the properties of the functions in (6):

- $J\big(x(t_i,p),p;\, i = 0, 1, \ldots, N\big)$ is once continuously differentiable with respect to $x(t_i,p)$, $i = 0, 1, \ldots, N$ and p on $\mathcal{R}^{n(N+1)} \times \mathcal{R}^r$.
- each element of $g_i\big(x(t_i,p),p\big), i = 0, 1, \ldots, N$, is once continuously differentiable with respect to $x(t_i,p)$ and p on $\mathcal{R}^n \times \mathcal{R}^r$.
- each element of $f(t,x,p)$ is continuous with respect to t and once continuously differentiable with respect to x and p on $\mathcal{I} \times \mathcal{R}^n \times \mathcal{R}^r$.
- each element of $x_0(p)$ is once continuously differentiable with respect to p on $\mathcal{R}^r$.
- $f(t,x,p)$ satisfies a uniqueness condition on $\mathcal{I} \times \mathcal{R}^n \times \mathcal{R}^r$.

The sequential approach is used for the solution of this dynamic optimization problem. The gradients

with respect to p can be evaluated using the parameter sensitivities. These are given from the solution of the sensitivity equations (Vassiliadis et al., 1994ab). Due to the generally non–convex nature of the functions used in the formulation of the dynamic optimization problem, the solution obtained using the sequential approach and a standard gradient–based NLP technique, is a local optimum and therefore provides an upper bound for the global optimum solution.

3. CONVEX RELAXATION OF PROBLEM

As it was mentioned before, BB algorithms are operating with concept of relaxations. In this section we briefly describe a possible convex relaxation presented in Papamichail and Adjiman (2002) of the non–convex dynamic optimization problem that was introduced in the previous section. The solution of this convex relaxation problem provides a lower bound for the global optimum of the non–convex problem. First, we reformulate the NLP problem (6) as

$$\begin{aligned} \min_{\hat{x},p}\ & J(\hat{x},p) \\ \text{s.t. } & g_i(\hat{x}_i,p) \le 0 \qquad i=0,1,\ldots,N \\ & \hat{x}_i = x(t_i,p) \qquad i=0,1,\ldots,N \\ & p \in [p^L,p^U] \end{aligned} \tag{7}$$

where $\hat{x}$ is a vector of new added optimized variables and values of $x(t_i,p), i=0,1,\ldots,N$ are obtained from the solution of the IVP

$$\begin{aligned} \dot{x} &= f(t,x,p) \qquad \forall t \in \mathcal{I} \\ x(t_0,p) &= x_0(p) \end{aligned} \tag{8}$$

3.1 *Bounding Variables and Solution of IVP*

It is very useful and in many cases essential to have bounds on variables, which are participating in optimization problem. For case of problem (7) bounds on parameters p are user–defined and bounds on variables $\hat{x}_i$ can depend just on bounds of these parameters. Within the generation of bounds on $\hat{x}_i$, which will definitely replace the presence of dynamic information in (7), relaxation of dynamic information will be formed. The dependence of convex relaxations on variable bounds is a common feature of deterministic global optimization algorithms. Since state variables appear in the non–convex objective function and constraints, a method for the derivation of rigorous bounds on these variables at point $t_i, i = 0,1,\ldots,N$, is needed. This issue can be resolved by generating bounds on the solution space of the dynamic system. Lower and upper parameter independent bounds can be determined for the solution $x(t,p)$ of IVP (8) such that $\underline{x}(t) \le x(t,p) \le \bar{x}(t)$, $\forall p \in [p^L,p^U]$, $\forall t \in \mathcal{I}$ where the inequalities are understood component–wise. Considering the assumptions and theorem given in Papamichail and Adjiman (2002) it can be assumed that, if f is continuous and satisfies a uniqueness condition on $\mathcal{I}_0 \equiv (t_0,t_N] \times \mathcal{R}^n \times [p^L,p^U]$, then the solution $\underline{x}(t)$ and $\bar{x}(t)$ of the following IVP satisfies

$$\begin{aligned} \dot{\underline{x}}_k &= \inf f_k(t,\underline{x}_k,[\underline{x}_{k-},\bar{x}_{k-}],[p^L,p^U]) \\ &\quad \forall t \in \mathcal{I} \quad k=1,2,\ldots,n \\ \underline{x}(t_0) &= \inf x_0([p^L,p^U]) \\ \dot{\bar{x}}_k &= \sup f_k(t,\bar{x}_k,[\underline{x}_{k-},\bar{x}_{k-}],[p^L,p^U]) \\ &\quad \forall t \in \mathcal{I} \quad k=1,2,\ldots,n \\ \bar{x}(t_0) &= \sup x_0([p^L,p^U]) \end{aligned} \tag{9}$$

These IVPs provide a practical procedure to construct bounding trajectories for IVP (8) if the appropriate continuity and uniqueness conditions are satisfied. Natural interval extensions are used as inclusion functions (Nickel, 1986).

3.2 *Convex Relaxation of Dynamic Information*

The set of equalities in (7) can be written as two sets of inequalities

$$\begin{aligned} \hat{x}_i - x(t_i,p) &\le 0 \qquad i=0,1,\ldots,N \\ x(t_i,p) - \hat{x}_i &\le 0 \qquad i=0,1,\ldots,N \end{aligned} \tag{10}$$

Their relaxation is given by

$$\hat{x}_i + \breve{x}^-(t_i,p) \le 0 \qquad i=0,1,\ldots,N \tag{11}$$

$$\breve{x}(t_i,p) - \hat{x}_i \le 0 \qquad i=0,1,\ldots,N \tag{12}$$

where $\breve{x}$ denotes the convex underestimator of the specified function and $x^-(t_i,p) = -x(t_i,p)$. Thus, the function $\breve{x}(t_i,p)$ is a convex underestimator of $x(t_i,p)$ and the function $-\breve{x}^-(t_i,p)$ is a concave overestimator of $x(t_i,p)$. The generation of these under and overestimators is the most challenging step in the construction of the convex relaxation of the problem because no analytical form is available for $x(t_i,p)$. The constant bounds are given by inequalities

$$\underline{x}(t_i) \le \hat{x}_i \le \bar{x}(t_i) \qquad i=0,1,\ldots,N \tag{13}$$

These inequalities are valid convex underestimators and concave overestimators for $x(t_i,p)$ and therefore they can replace inequalities (11) and (12). These bounds do not depend on the parameters p themselves, but do depend on the bounds on p.

3.3 *Convex Relaxation of the NLP*

After underestimating the objective function and overestimating the feasible region, the convex relaxation of the NLP problem (7) is given by

$$\begin{aligned}
\min_{\hat{x},p,w}\ & \breve{J}(\hat{x},p,w)\\
\text{s.t. } & \breve{g}_i(\hat{x}_i,p,w)\le 0 \qquad i=0,1,\ldots,N\\
& \underline{x}(t_i)\le \hat{x}_i\le \bar{x}(t_i) \quad i=0,1,\ldots,N\\
& \mathcal{C}(\hat{x},p,w)\le 0\\
& p\in[p^L,p^U]
\end{aligned} \tag{14}$$

where $\breve{J}$ denotes the convex underestimator of the specified function, $\mathcal{C}$ denotes the set of additional constraints arising from the convex relaxation of non–convex terms of special types and w denotes the vector of new variables introduced by this relaxation.

4. EXAMPLES

The global optimization algorithm presented in Papamichail and Adjiman (2004) was implemented using MATLAB 6.5. To obtain the bounds on variables we used the constant bounds approach (see section 3.2). This technique is relatively simple, but suitable for the examples solved in this work.

Solution of NLP problems was found using function *fmincon*. It is an implementation of a general NLP solver, provided by the Optimization Toolbox, uses either a subspace trust region method, based on the interior–reflective Newton method, or a sequential quadratic programming method. The MATLAB function *ode45* was used for the integration of IVPs. It is an implementation of a Runge–Kutta method based on the Dormand–Prince pair. The interval calculations needed were performed explicitly using interval arithmetic. Interval arithmetic computations are shown for each example. First example is a simple dynamic optimization problem. The next three examples are parameter estimation problems in chemical kinetics modeling. All the case studies were solved on a workstation Dell Optiplex GX250, 3 GHz Intel Pentium 4 CPU with 1GB RAM.

4.1 *Example 1: Irreversible Liquid–phase Reaction of the First Order*

First example is a parameter estimation problem with two parameters and two differential equations as the constraints. It was published in Esposito and Floudas (2000) as well as in Papamichail and Adjiman (2002). It involves a first–order irreversible isothermal liquid–phase chain reaction.

$$\mathrm{A} \overset{k_1}{\rightarrow} \mathrm{B} \overset{k_2}{\rightarrow} \mathrm{C}$$

The problem can be formulated as follows:

$$\begin{aligned}
\min_{k_1,k_2}\ & \sum_{j=1}^{10}\sum_{i=1}^{2}(x_i(t=t_j,k_1,k_2)-x_i^{\exp}(t_j))^2\\
\text{s.t. } & \dot{x}_1=-k_1x_1 \qquad \forall t\in[0,1]\\
& \dot{x}_2=k_1x_1-k_2\,x_2 \qquad \forall t\in[0,1]\\
& x_1(t=0,k_1,k_2)=1\\
& x_2(t=0,k_1,k_2)=0\\
& 0\le k_1\le 10\\
& 0\le k_2\le 10
\end{aligned} \tag{15}$$

where x_1 and x_2 are the mole fractions of components A and B, respectively. k_1 and k_2 are the rate constants of the first and second reaction, respectively. $x_i^{\exp}(t_j)$ is the experimental point for the state variable i at time t_j. The points used are taken from Esposito and Floudas (2000).

Applying the procedure defined by (9) leads to the expressions

$$\begin{aligned}
&\dot{\underline{x}}_1=\inf(-[k_1^L,k_1^U]\times\underline{x}_1) \quad \forall t\in[0,1]\\
&\underline{x}_{10}=\inf x_{10}([p^L,p^U])\\
&\dot{\underline{x}}_2=\inf([k_1^L,k_1^U]\times[\underline{x}_1,\bar{x}_1]-\\
&\qquad -[k_2^L,k_2^U]\times\underline{x}_2) \quad \forall t\in[0,1]\\
&\underline{x}_{20}=\inf x_{20}([p^L,p^U])
\end{aligned} \tag{16}$$

$$\begin{aligned}
&\dot{\bar{x}}_1=\sup(-[k_1^L,k_1^U]\times\bar{x}_1) \quad \forall t\in[0,1]\\
&\bar{x}_{10}=\sup x_{10}([p^L,p^U])\\
&\dot{\bar{x}}_2=\sup([k_1^L,k_1^U]\times[\underline{x}_1,\bar{x}_1]-\\
&\qquad -[k_2^L,k_2^U]\times\bar{x}_2) \quad \forall t\in[0,1]\\
&\bar{x}_{20}=\sup x_{20}([p^L,p^U])
\end{aligned} \tag{17}$$

which using the interval arithmetic calculation results in four bounding IVPs

$$\begin{aligned}
&\dot{\underline{x}}_1=-k_1^U\underline{x}_1 \quad \forall t\in[0,1]\\
&\underline{x}_{10}=1\\
&\dot{\underline{x}}_2=k_1^L\underline{x}_1-k_2^U\underline{x}_2 \quad \forall t\in[0,1]\\
&\underline{x}_{20}=0
\end{aligned} \tag{18}$$

$$\begin{aligned}
&\dot{\bar{x}}_1=-k_1^L\bar{x}_1 \quad \forall t\in[0,1]\\
&\bar{x}_{10}=1\\
&\dot{\bar{x}}_2=k_1^U\bar{x}_1-k_2^L\bar{x}_2 \quad \forall t\in[0,1]\\
&\bar{x}_{20}=0
\end{aligned} \tag{19}$$

Solutions of these ODEs represent a convex underestimator and concave overestimator of the relaxed problem solution space.

The global optimization algorithm converged with the relative convergence criterion ϵ_r set to 1×10^{-2}. The global optimum parameter found was $k_1=5.0035$ and $k_2=1.0000$ and the value of the objective function for the global optimum parameter was equal to 1.1856×10^{-6}. 3436 iterations were necessary for convergence of the algorithm in 2632 seconds. The experimental points and trajectories of state variables for global optimum are shown in Fig. 1. The upper bound calculation was performed once every 100 iterations.

Results show that for this problem with simple dynamics and only two parameters, algorithm is efficient and quite fast while we need less than one

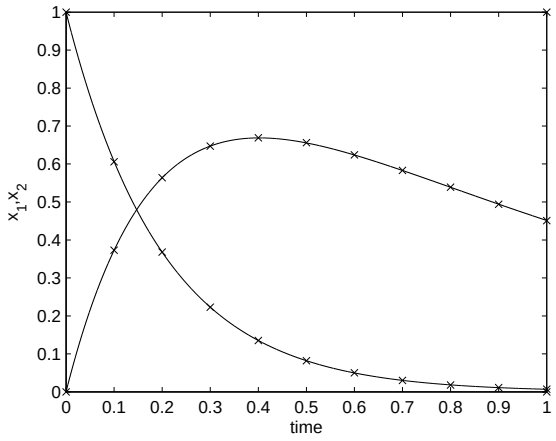

Fig. 1. Experimental points and state variable trajectories for the globally optimal parameters in Example 2

hour to obtain a solution. This is because data was generated using integration of system with parameter values $k = [5, 1]$ with no error added.

4.2 *Example 2: Catalytic Cracking of Gas Oil*

This example is a parameter estimation problem with three parameters and two differential equations in the constraints. It appears in Esposito and Floudas (2000) and Papamichail and Adjiman (2004). It involves an overall reaction of catalytic cracking of gas oil (A) to gasoline (Q) and other products (S):

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_1} \mathrm{Q} \\ \mathrm{Q} &\xrightarrow{k_2} \mathrm{S} \\ \mathrm{A} &\xrightarrow{k_3} \mathrm{S} \end{aligned}$$

The problem is formulated as follows:

$$\begin{aligned} \min_{k_1,k_2,k_3} \; & \sum_{j=1}^{20}\sum_{i=1}^{2}(x_i(t=t_j,k_1,k_2,k_3) - x_i^{\exp}(t_j))^2 \\ \text{s.t. } & \dot{x}_1 = -(k_1+k_3)x_1^2 \qquad \forall t \in [0, 0.95] \\ & \dot{x}_2 = k_1 x_1^2 - k_2 x_2 \qquad \forall t \in [0, 0.95] \\ & x_1(t=0,k_1,k_2,k_3) = 1 \\ & x_2(t=0,k_1,k_2,k_3) = 0 \\ & 0 \le k_1 \le 20 \\ & 0 \le k_2 \le 20 \\ & 0 \le k_3 \le 20 \end{aligned} \tag{20}$$

where x_1 and x_2 are the mole fractions of components A and Q, respectively. k_1, k_2, and k_3 are the rate constants of the respective reactions. $x_i(t_j)$ is the experimental measurement for the state variable i at time t_j. The measurement points used are again taken from Esposito and Floudas (2000).

Applying the procedure defined by (9) and using the interval arithmetic calculation resulted in following bounding IVPs

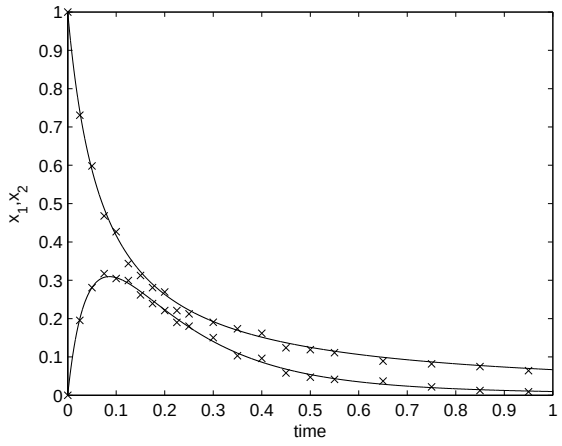

Fig. 2. Experimental points and state variable trajectories for the globally optimal parameters in Example 3

$$\begin{aligned} & \dot{\underline{x}}_1 = -(k_1^U + k_3^U)\underline{x}_1^2 \quad \forall t \in [0, 0.95] \\ & \underline{x}_{10} = 1 \\ & \dot{\underline{x}}_2 = k_1^L \underline{x}_1^2 - k_2^U \underline{x}_2 \quad \forall t \in [0.95] \\ & \underline{x}_{20} = 0 \end{aligned} \tag{21}$$

$$\begin{aligned} & \dot{\bar{x}}_1 = -(k_1^L + k_3^L)\bar{x}_1^2 \quad \forall t \in [0, 0.95] \\ & \bar{x}_{10} = 1 \\ & \dot{\bar{x}}_2 = k_1^U \bar{x}_1^2 - k_2^L \underline{x}_2 \quad \forall t \in [0, 0.95] \\ & \bar{x}_{20} = 0 \end{aligned} \tag{22}$$

Solutions of these ODEs represent a convex underestimator and concave overestimator of the relaxed problem solution space.

The globally optimal parameters are $k_1 = 12.2111$, $k_2 = 7.9764$, and $k_3 = 2.2259$ with the corresponding value of the objective function equal to 2.655×10^{-3}, when convergence criterion is set to 1×10^{-2}. The experimental points and the state variable trajectories for the global optimum are shown in Fig. 4.2. Algorithm converged after 8497 iterations and 13637 seconds of CPU time. The upper bound calculation was performed once every 100 iterations.

In this example with non–linear dynamic system and three parameters to be estimated, rise of the computational effort is significant. This can be contributed to the higher complexity of the problem and also to small amount of random error added to the data integrated for parameters $k = [12, 8, 2]$, which is evident from value of the objective function in optimum.

4.3 *Example 3: Reversible Liquid–phase Reaction of the First Order*

The third example is a parameter estimation problem with four parameters and three differential equations. It appears in Esposito and Floudas (2000). It involves a first–order reversible isothermal liquid–phase chain reaction.

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{C}$$

The problem can be formulated as follows:

$$\begin{aligned}
&\min_{\substack{k_1,k_2,\\ k_3,k_4}} \sum_{j=1}^{20}\sum_{i=1}^{3}(x_i(t=t_j,k_1,k_2,k_3,k_4) - x_i^{\exp}(t_j))^2 \\
&\text{s.t. } \dot{x}_1 = -k_1x_1 + k_2x_2 \qquad \forall t \in [0,1] \\
&\quad \dot{x}_2 = k_1x_1 - (k_2+k_3)x_2 + k_4x_3 \\
&\qquad\qquad\qquad\qquad \forall t \in [0,1] \\
&\quad \dot{x}_3 = k_3x_2 - k_4x_3 \qquad \forall t \in [0,1] \\
&\quad x_1(t=0,k_1,k_2,k_3,k_4) = 1 \\
&\quad x_2(t=0,k_1,k_2,k_3,k_4) = 0 \\
&\quad x_3(t=0,k_1,k_2,k_3,k_4) = 0 \\
&\quad 0 \le k_1 \le 10 \\
&\quad 0 \le k_2 \le 10 \\
&\quad 10 \le k_3 \le 50 \\
&\quad 10 \le k_4 \le 50
\end{aligned} \tag{23}$$

where x_1, x_2, and x_3 are the mole fractions of components A, B and, C, respectively. k_1, k_2, and k_3 are the rate constants of the first and second reaction, respectively. $x_i(t_j)$ is the experimental point for the state variable i at time t_j. The points used are taken from Esposito and Floudas (2000).

Applying the procedure defined by (9) leads to the expressions which using the interval arithmetic calculation resulted in six bounding IVPs

$$\begin{aligned}
&\dot{\underline{x}}_1 = -k_1^U\underline{x}_1 + k_2^U\underline{x}_2 \quad \forall t \in [0,1] \\
&\underline{x}_{10} = 1 \\
&\dot{\underline{x}}_2 = k_1^L\underline{x}_1 - (k_2^U + k_3^U)\underline{x}_2 + \\
&\qquad +k_4^L\underline{x}_3 \quad \forall t \in [0,1] \\
&\underline{x}_{20} = 0 \\
&\dot{\underline{x}}_3 = k_3^L\underline{x}_2 - k_4^U\underline{x}_3 \quad \forall t \in [0,1] \\
&\underline{x}_{30} = 0
\end{aligned} \tag{24}$$

$$\begin{aligned}
&\dot{\bar{x}}_1 = -k_1^L\bar{x}_1 + k_2^U\bar{x}_2 \quad \forall t \in [0,1] \\
&\bar{x}_{10} = 1 \\
&\dot{\bar{x}}_2 = k_1^U\underline{x}_1 - (k_2^L + k_3^L)\bar{x}_2 + \\
&\qquad +k_4^U\bar{x}_3 \quad \forall t \in [0,1] \\
&\bar{x}_{20} = 0 \\
&\dot{\bar{x}}_3 = k_3^U\bar{x}_2 - k_4^L\bar{x}_3 \quad \forall t \in [0,1] \\
&\bar{x}_{30} = 0
\end{aligned} \tag{25}$$

Solutions of these ODEs represent a convex underestimator and concave overestimator of the relaxed problem solution space.

The experimental points and trajectories of state variables for global optimum are shown in Fig. 3.

Algorithm converged within the relative convergence criterion ϵ_r set to 1×10^{-2}. Global optimum found was with parameter values $k_1 = 3.9990$, $k_2 = 1.9981$, $k_3 = 40.0000$ $k_4 = 20.0007$, and the value of the objective function for the global optimum parameter was equal to 1.1856×10^{-6}. Algorithm converged after 44600 iterations and 142380 seconds of CPU time. The upper bound

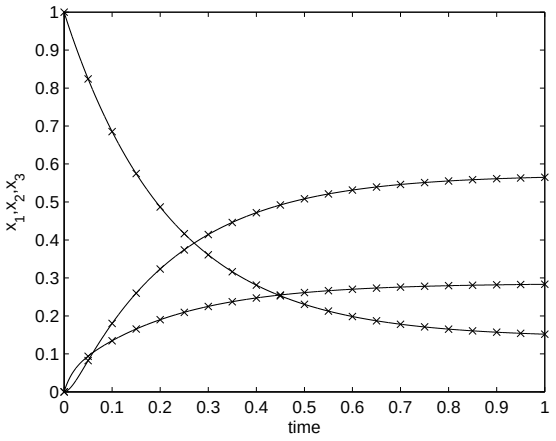

Fig. 3. Experimental points and state variable trajectories for the globally optimal parameters in Example 4

calculation was performed once every 100 iterations.

Despite that there was no random error added to integrated data for parameters $k = [4, 2, 40, 20]$ and system with linear dynamic embedded was studied, there is an enormous increase of computational time needed (almost 2 days). According to examples discussed previously the only explanation of this lies in augmented number of parameters together with extended parameter ranges.

5. CONCLUSION AND FUTURE WORK

Main purpose of this work was to present application of a global optimization algorithm suitable for parameter estimation problems of dynamic systems. A deterministic sBB global optimization algorithm was employed. Local solutions produced using the sequential approach were used as an upper bound on the global minimum of the objective function value. Lower bounds were provided from the solution of a convex relaxation of the problem on subregions considered in the BB algorithm. This convex relaxation was achieved after defining a convex underestimation of the objective function and a convex overestimation of the feasible region.

We implemented the algorithm proposed by Papamichail and Adjiman (2004) and used it to solve selected examples relevant to chemical engineering. The principle of constant bounds is very useful and also quite simple. Although there are some other few methods (affine bounds, αBB–bounds) already developed, we focused on this approach in the work. Explicit interval arithmetic calculations were used and solution of IVP (9) was performed once at each node of BB tree. Results show that the method of constant bounds for larger problems results in enormous rise of the number of iterations and computation time needed to obtain the global optimum. These results suggest that

future work should be focused on larger systems with utilization of different bounding strategies.

ACKNOWLEDGMENTS

The work has been supported by the Scientific Grant Agency of the Slovak Republic under the grants 1/0071/09 and 1/4055/07 and by the Slovak Research and Development Agency under the contract No. VV-0029-07. This support is very gratefully acknowledged.

References

C. S. Adjiman, I. P. Androulakis, C. D. Maranas, and C. A. Floudas. A global optimization method, αBB for process design. *Computers and Chemical Engineering*, 20:419–424, 1996.

M. Bagajewicz and V. Manousiouthakis. On the generalized Benders decomposition. *Computers and Chemical Engineering*, 15:691–700, 1991.

W. Esposito and C. Floudas. Global optimization for the parameter estimation of differential-algebraic systems. *Industrial and Engineering Chemistry Research*, 39:1291–1310, 2000.

C.A. Floudas and V. Visweswaran. A global optimization algorithm (GOP) for certain classes of non-convex NLPs – I theory. *Computers and Chemical Engineering*, 14:1397–1417, 1990.

A. M. Geoffrion. Generalized Benders decomposition. *Journal of Optimization Theory and Applications*, 10:237–260, 1972.

J. R. Han, V. Manousiouthakis, and S. H. Choi. Global optimization of chemical processes using the interval analysis. *Korean Journal of Chemical Engineering*, 14:270–276, 1997.

K. L. Nickel. Using interval methods for numerical solution of ODE's. *ZAMM*, 66(11):513–523, 1986.

I. Papamichail and C. S. Adjiman. A rigorous global optimization algorithm for problems with ordinary differential equations. *Journal of Global Optimization*, 24:1–33, 2002.

I. Papamichail and C. S. Adjiman. Global optimization of dynamic systems. *Computers and Chemical Engineering*, 28:403–415, 2004.

H. Ratschek and J. Rokne. *New Computer Methods for Global Optimization*. Ellis Horwood, Chichester, England, 1988.

H. S. Ryoo and N. V. Sahinidis. Global optimization of nonconvex NLPs and MINLPs with applications in process design. *Computers and Chemical Engineering*, 19:551–566, 1995.

R. M. Soland. An algorithm for separable nonconvex programming problems II: Nonconvex constraints. *Management Science*, 17:759–773, 1971.

R. Vaidyanathan and M. El-Halwagi. Global optimization of nonconvex nonlinear programs via interval analysis. *Computers and Chemical Engineering*, 18:889–897, 1994.

V. S. Vassiliadis, R. W. H. Sargent, and C. C. Pantelides. Solution of a class of multistage dynamic optimization problems. 1. problems without path constraints. *Industrial and Engineering Chemistry Research*, 33(9):2111–2122, 1994a.

V. S. Vassiliadis, R. W. H. Sargent, and C. C. Pantelides. Solution of a class of multistage dynamic optimization problems. 2. problems with path constraints. *Industrial and Engineering Chemistry Research*, 33(9):2123–2133, 1994b.

M. Čižniar, M. Podmajerský, T. Hirmajer, M. Fikar, and M. A. Latifi. Global optimization for the parameter estimation of differential-algebraic systems. *Chemical Papers*, 2009. (accepted).