# An Efficient RTO Scheme for the Optimal Operation of Chemical Processes Under Uncertainty

Reinaldo Hernández, Monika Bucková, Sebastian Engell Faculty of Biochemical and Chemical Engineering Process Dynamics and Operations Group TU Dortmund Dortmund, Germany Email: reinaldo.hernandez@bci.tu-dortmund.com

Abstract---In this contribution, an efficient Real-time Optimization (RTO) scheme for the optimal operation of chemical processes under uncertainty is proposed. This work builds on two recently published iterative robust optimization methodologies: Modifier Adaptation with Quadratic Approximation (MAWQA) and Directional Modifier Adaptation (DMA) and proposes a unified framework where the benefits of both methods are combined. As a consequence, fast convergence to the true plant optimum is achieved despite the presence of plant-model mismatch. The methodology is illustrated by simulation studies of a novel transition metal complex catalyzed process.

#### I. INTRODUCTION

Nowadays the process industry faces multiple challenge including an increasing global competition, high quality standards and tight environmental regulations. Model-based Real-time Optimization (RTO) has emerged as an attractive approach to improve the efficiency of plant operations [1]. The key idea in RTO schemes is to make use of a stationary nonlinear, usually first principles based mathematical model of the plant, with the goal of operating the process as closely as possible to its optimum. Despite the increasing acceptance of RTO in refineries and petrochemical processes like Fluid Catalytic Cracking or Steam Cracking, its application to other processes is still limited. This can be partially explained by the fact that under model inaccuracies (i.e. plant-model mismatch), convergence to the true plant optimum cannot be ensured or it might lead to constraint violations. On the other hand, the effort needed to develop very accurate first principles plant models is a bottleneck for the application of advanced model-based solutions.

In the classical RTO scheme, the issue of plant-model mismatch is usually addressed by online adaptation of some model parameters. This however will only resolve the problem if the model is structurally correct. A different approach to address the issue of plant-model mismatch is the addition of gradients and bias correction terms to the objective function and to the constraints of the nominal optimization problem in the so-called Modifier Adaptation scheme [2], [3], [4]. Under the assumption of model adequacy [5], it has been shown that the algorithm generates a sequence of inputs that converges to a stationary point of the plant. The main challenge of this method is the accurate estimation of the

plant gradients. In the seminal work of [6], the approximation of the derivatives by finite differences was proposed, which limits the method to low-dimensional problems with negligible noise levels. More sophisticated algorithms have been proposed during the last years including dual Modifier Adaptation (Dual-MA) [7], Nested Modifier Adaptation [8], and more recently the use of ideas from the derivative free-optimization (DFO) framework in the Modifier Adaptation with Quadratic Approximation (MAWQA scheme) [9]. While the robustness of these methods has been demonstrated under structural mismatch and in the presence of noisy measurements, for quite a few examples, in the case of several inputs that are included in the optimization, the number of necessary plant trials can be large. In [10] the concept of directional derivatives within the context of Modifier Adaptation (Directional Modifier Adaptation, DMA) was introduced with the aim of reducing the number of perturbation directions by performing only moves that yield significant information based on a parametric sensitivity analysis. In the same work the method was combined with Dual-MA and applied to a power kite.

In this work, a new RTO scheme is proposed for the optimal operation of chemical processes under model uncertainty and noisy measurements. The methodology combines the benefits of MAWQA and DMA in a unified framework with an improved robustness to measurement noise, while at the same time the number of functions evaluations (plant perturbations) is reduced. The paper is organized as follows. In section II the problem is stated. The proposed scheme is presented in section III. The case study is introduced in section IV, and the resulting problem is stated in section V. Simulation results are presented in section VI. Finally, some concluding remarks are given in section VII.

# II. PROBLEM STATEMENT

RTO can be stated as a static optimization problem:

$$\begin{array}{ll} \min_{\mathbf{u}} & J_p(\mathbf{u}) \\ \text{s.t.} & \mathbf{C}_p(\mathbf{u}) \leq 0 \\ & \underline{\mathbf{u}} \leq \mathbf{u} \leq \overline{\mathbf{u}}, \end{array}$$
(1)

where the vector of manipulated variables  $\mathbf{u} \in \mathbf{R}^n$  is bounded by  $\underline{\mathbf{u}}$  and  $\overline{\mathbf{u}}$ ,  $J_p(\mathbf{u}) \colon \mathbf{R}^n \to \mathbf{R}$  is a scalar objective function

TABLE I Algorithm Modifier Adaptation

Algorithm Modifier-Adaptation				
<b>Step 1:</b> Given the initial point $\mathbf{u}^0$ , set $k = 0$				
<b>Step 2:</b> Calculate the modifiers according to (4)				
<b>Step 3:</b> Compute the next input by solving (3)				
<b>Step 4:</b> Set $k \leftarrow k+1$ , return to <b>Step 2</b>				

of the plant, and  $\mathbf{C}_p(\mathbf{u}) \colon \mathbf{R}^n \to \mathbf{R}^r$  is a vector of plant constraints. In practice, the true process mapping is not known, and only approximations of the objective function  $(J_m)$  and of the constraints  $(\mathbf{C}_m)$  are available. Then, the nominal optimization problem can be stated as:

$$\begin{array}{ll} \min_{\mathbf{u}} & J_m(\mathbf{u}) \\ \text{s.t.} & \mathbf{C}_m(\mathbf{u}) \leq 0 \\ & \underline{\mathbf{u}} \leq \mathbf{u} \leq \overline{\mathbf{u}}. \end{array}$$
(2)

The goal is to determine the vector of inputs  $\mathbf{u}^*$  which satisfies the optimality conditions of (1) by using measurements of the values of the cost function and of the constraints that are observed at the real plant together with the nominal model in (2).

# III. METHOD PROPOSED

#### A. Modifier Adaptation

The idea behind Modifier Adaptation (MA) is to add bias and gradient correction terms to (2), resulting in an iterative optimization procedure:

$$\mathbf{u}^{k+1} = \underset{\mathbf{u}}{\operatorname{argmin}} \quad J_m(\mathbf{u}) + \epsilon_J^{(k)} + \boldsymbol{\lambda}_J^{(k)} \left(\mathbf{u} - \mathbf{u}^{(k)}\right)$$
  
s.t. 
$$\mathbf{C}_m(\mathbf{u}) + \boldsymbol{\epsilon}_{\mathbf{C}}^{(k)} + \boldsymbol{\lambda}_{\mathbf{C}}^{(k)} \left(\mathbf{u} - \mathbf{u}^{(k)}\right) \leq 0 \quad (3)$$
$$\underline{\mathbf{u}} \leq \mathbf{u} \leq \overline{\mathbf{u}}.$$

The superscript k denotes the iteration number. The bias is corrected by the zeroth-order modifiers  $\epsilon$  while the gradient correction is done by the first-order modifiers  $\lambda$ :

$$\begin{aligned} \boldsymbol{\epsilon}_{J}^{(k)} &= J_{p}^{(k)} - J_{m}^{(k)} \\ \boldsymbol{\lambda}_{J}^{(k)} &= \left(\nabla J_{p}^{(k)} - \nabla J_{m}^{(k)}\right)^{T} \\ \boldsymbol{\epsilon}_{\mathbf{C}}^{(k)} &= \mathbf{C}_{p}^{(k)} - \mathbf{C}_{m}^{(k)} \\ \boldsymbol{\lambda}_{\mathbf{C}}^{(k)} &= \left(\nabla \mathbf{C}_{p}^{(k)} - \nabla \mathbf{C}_{m}^{(k)}\right)^{T}. \end{aligned}$$

$$(4)$$

The modifier adaptation scheme can be summarized in the algorithm presented in Table I [11]:

**Proposition:** Assume a perfect estimation of the plant gradients; also assume that the iterative scheme (3) converges to the point  $\mathbf{u}^{\infty}$ . If this point is a KKT point of the modified problem (3), then  $\mathbf{u}^{\infty}$  is also a KKT of the plant (1).**Proof:** the proof is straightforward, as follows that the substitution of  $\mathbf{u}^{\infty}$  in the first-order optimality conditions of the modified problem (3) implies the first-order optimality conditions of the plant. It is important to note that the algorithm can converge to any stationary point (including a saddle point) of the plant.

For further details of the convergence properties of MA, the reader is referred to [5].

# B. Modifier Adaptation with Quadratic Approximation (MAWQA)

The most challenging aspect of MA is the accurate estimation of the plant gradients. The seminal work of [6] suggested introducing perturbations around the current operating point with the aim of approximating the derivatives by finite differences. However, firstly this leads to additional set point changes which may not be welcomed by the plant operators and secondly, the choice of the size of the perturbation is difficult in the presence of measurement noise [3]. A recently proposed approach [9] makes use of quadratic approximation as it is used in the derivative-free optimization framework; the basic idea is the estimation of the process gradients by fitting a quadratic model to the data that was obtained at previously visited operating points. The quadratic approximation of the objective function is defined as:

$$J_{\phi}(\mathbf{u}, \boldsymbol{\pi}) = \sum_{i=1}^{n_u} \sum_{j=1}^{n_u} a_{i,j} u_i u_j + \sum_{i=1}^{n_u} b_i u_i + c, \qquad (5)$$

with the parameter set  $\pi = \{a_{1,1}, \dots, a_{n_u,n_u}, b_1, \dots, b_{n_u}, c\}$ obtained from solving the least-squares problem

$$\min_{\boldsymbol{\pi}} \sum_{i=1}^{n_r} \left( J_p\left(\mathbf{u}^{(r_i)}\right) - J_\phi\left(\mathbf{u}^{(r_i)}, \boldsymbol{\pi}\right) \right)^2, \qquad (6)$$

where  $\mathbf{u}^{(r_i)}$  is an element of the regression set  $\mathcal{U}^{(k)}$  composed of past set-points selected to guarantee well-poisedness of the problem. A minimum of (n + 1)(n + 2)/2 points must be collected before  $J_{\phi}$  can be computed. The values of the constraint functions are approximated in a similar fashion. Instead of introducing additional perturbations to the process, MAWQA computes the plant derivatives from the derivatives of the quadratic model. The new set-point obtained from the solution of (3) is additionally restricted by an elliptical trust region which is defined by the covariance of the regression set. The algorithm is presented in detail in [9].

#### C. Directional Modifier Adaptation (DMA)

In order to reduce the number of functions evaluations under parametric uncertainties, the use of directional derivatives has recently been proposed [10]. The basic idea is to perturb the process only in the directions according to the largest variation of the gradient of the Lagrangian L with respect to a set of uncertain model parameters  $\theta$  in the model. The first step in the algorithm involves the computation of the influence of the normalized parameter variations on the gradient of the Lagrangian, represented by the matrix M:

$$\mathbf{M} = \frac{\partial^2 L}{\partial \mathbf{u} \partial \theta} (\mathbf{u}^*, \nu^*, \theta_0)$$

$$\times diag(\theta_1^{max} - \theta_1^{min}, \dots \theta_{n_\theta}^{max} - \theta_{n_\theta}^{min}).$$
(7)

M is computed at the nominal (model) optimal operating point  $\mathbf{u}^*$ , with multipliers  $\nu^*$  and the nominal parameter

values  $\theta_0$ . In order to normalize the sensitivities, it is assumed that the minimum and maximum parameter values ( $\theta_i^{max}$ ,  $\theta_i^{min}$ ) are known. The SVD generates the matrices  $\mathbf{U}, \boldsymbol{\Sigma}$ and  $\mathbf{V}$ , according to  $\mathbf{M} = \mathbf{U}\boldsymbol{\Sigma}\mathbf{V}^T$ . The matrix  $\mathbf{M}$  can be approximated by a lower rank matrix  $\mathbf{M}$  as stated in the Eckart-Young-Mirsky theorem:

$$\tilde{\mathbf{M}} = \mathbf{U}\tilde{\boldsymbol{\Sigma}}\mathbf{V}^T,\tag{8}$$

where  $\hat{\Sigma}$  is a diagonal matrix that contains only the  $n_r < n$  largest singular values, while the other singular values are set to zero. The quality of the approximation given by (8) depends on the condition number of  $\Sigma$ , i.e. given a singular value  $\sigma_j << \sigma_1$ , then neglecting the vector corresponding to  $\sigma_j$  will have a low impact in terms of optimality loss. As a result, a low-rank approximation of U given by  $U_r$  is obtained where the columns of  $U_r$  corresponds to the preferred directions. Then the computation of the directional derivatives is straightforward. This is illustrated for the case of the plant objective function:

$$\nabla_{\mathbf{U}_{\mathbf{r}}} J_p^{(k)} = \frac{\partial J_p(\mathbf{u}^{(\mathbf{k})} + \mathbf{U}_{\mathbf{r}}\mathbf{r})}{\partial \mathbf{r}},\tag{9}$$

where **r** is the vector of dimension  $n_r$ . Based on the directional derivatives, the plant gradients can be estimated as:

$$\nabla J_p^{(k)} = \nabla J_m^{(k)} \left( \mathbf{I_n} - \mathbf{U_r} \mathbf{U_r^+} \right) + \nabla_{\mathbf{U_r}} J_p^{(k)} \mathbf{U_r^+}, \qquad (10)$$

where  $\mathbf{U}_{\mathbf{r}}^+$  is the pseudo inverse of  $\mathbf{U}_{\mathbf{r}}$ . Equation (10) ensures that the model derivatives are used in those directions of  $\mathbf{U}$ that were neglected in  $\mathbf{U}_{\mathbf{r}}$ , while the directional derivatives are projected in those directions that are within the column space of  $\mathbf{U}_{\mathbf{r}}$ .

# D. Combining MAWQA and DMA

In order to combine the advantages of both methods for multivariable stationary optimization problems under uncertainty, the following procedure is proposed:

Step 1: Off-line computations of sensitivities. Given the nominal optimal point  $\mathbf{u}^0$ , and the nominal parameters and bounds, the sensitivity analysis represented by (7) is performed and the matrix  $\mathbf{U}_{\mathbf{r}}$  is obtained from (8). Set k = 0

**Step 2: Perturbation of the process in the sensitive directions.** The directional derivatives are computed according to (9) and the estimated plant gradients are obtained from (10).

Step 3: Compute a new operating point The optimization problem (3) is solved and the new operating point  $\mathbf{u}^{k+1}$  is obtained. If convergence criteria are satisfied, the algorithm finishes, otherwise set  $k \leftarrow k + 1$  and repeat steps (2)-(3) until a minimal number of (n+1)(n+2)/2 points have been collected (minimum required for MAWQA)

**Step 4: Modifier Adaptation with Quadratic Approximation.** The algorithm switches to MAWQA. i.e. the plant gradients are calculated from the regressed quadratic model (Equations (5)-(6)) [9]. Solve (3) with the calculated gradients until the convergence criterion has been satisfied.



Fig. 1. Thermomorphic Solvent System (TMS)

# IV. CASE STUDY: OPTIMAL OPERATION OF A TRANSITION METAL COMPLEX CATALYZED PROCESS

# A. Process Description

Transition metal complex catalysis (also known as organometallic catalysis) has become one of the most active research fields in industrial chemistry. The attainable high selectivity and activity at mild reaction conditions make them suitable in pharmaceutical and fine chemistry synthesis. This is illustrated by the fact that during the last 15 years, three Nobel prizes in chemistry (2001, 2005, 2010) have been awarded to researchers who have worked on this field. Furthermore, it has been suggested that organometallic catalysis is one of the fundamentals blocks in green chemistry, due to the minimization of by-products thanks to the high selectivity of the catalyst complex and its potential application on the processing of renewable raw material. Despite the aforementioned promising results, commercial applications of transition metal complex catalysis are still limited in comparison to their heterogeneous counterparts. The high price of the metals and ligands necessitates an efficient catalyst recovery concept. For processes with mass transfer limitations due to low solubility of at least one of the reactants or of the catalyst in the reaction mixture, the idea of exploiting the temperature dependence of the miscibility gap of a multicomponent solvent has been proposed [12].

The principle of a thermomorphic solvent system (TMS) is illustrated in figure 1. The feed (S3) is mixed with a carefully selected mixture of polar (S1) and nonpolar solvent (S2). At elevated temperature (T1) in the reactor the mixture is homogeneous and therefore mass transfer limitations between the two liquid phases are overcome; at a lower temperature (T2), phase separation takes place and the phase that contains the catalyst is recovered and recycled to the reactor. The product phase is sent to further processing stages for solvent separation and product purification. The process can be continuously operated as is shown in figure 2.

In this work, the model reaction of the hydroformylation of 1-dodecene to the linear aldehyde tridecanal using a Rhodium-Biphephos complex in a TMS system consisting of dymethlyformamide (DMF) and decane is studied. The process concept has been demostrated in the collaborative Research Center/Transregio 63 in a miniplant at TU Dortmund [13], [14]. Besides the main reaction, undesired isomerization



Fig. 2. Continuously operated TMS plant



Fig. 3. Reaction network for the hydroformylation of 1-dodecene

and hydrogenation take place; as it is shown in the reaction network (Figure 3). Therefore, the reaction conditions must be carefully chosen in order to maximize the selectivity towards the desirable product (the linear aldehyde). This process has benn used as a case study for the design of chemical processes under uncertainty [15]

#### B. Model Description

In this section a brief description of the process model is provided, for further details we refer the reader to [16]. According to the material balance, the concentrations of the different liquid components  $C_i$  (i = n-dodecene, n-tridecanal, dodecane, etc), are given by (11):

$$\dot{V}_{in}C_{i,in} - \dot{V}_{out}C_{i,out} - C_{cat}V_R \sum_{j=1}^{Nreac} \nu_{i,j}r_j = 0, \quad (11)$$

where  $C_{cat}$  is the concentration of active catalyst in the reactor with volume  $V_R$  and  $\dot{V}_{in}, \dot{V}_{out}$  are volumetric flows at the inlet and the outlet of the reactor,  $\nu_{i,j}$  are the coefficients in the stoichiometric matrix and  $r_j$  is the reaction rate for the jreaction. The kinetic model is described in detail in [17].

The two-film theory is used for the description of the mass transfer between the gas and liquid phases. The equilibrium at the interface G-L is described by means of Henry equations, where the relations between the liquid concentrations and the partial pressure  $P_i$  are assumed as linear. The dependency of the Henry coefficient  $H_i$  on the reaction temperature  $T_R$  is given by an Arrhenius expression, with activation energy  $E_i$ .

$$P_{i} = C_{i}^{eq} H_{i}$$

$$H_{i} = H_{i,0} \exp\left(\frac{-E_{i}}{RT_{R}}\right).$$
(12)

The bulk concentration of the gas components in the liquid phase depends on the mass transfer coefficient  $(k_{eff})$  and equilibrium concentration at the interface  $(C_i^{eq})$ :

$$-k_{eff}(C_i - C_i^{eq}) - V_{out}C_{i,out} - C_{cat}V_R \sum_{j=1}^{Nreac} \nu_{i,j}r_j = 0.$$
(13)

It is assumed that the LLE between the phases is reached in the decanter. Based on experimental values, simple expressions of the equilibrium constants  $K_i$  as functions of the decanter temperature for the different liquid components *i* were obtained:

$$K_{i} = \exp\left(A_{i,0} + \frac{A_{i,1}}{T_{decanter}} + A_{i,2}T_{decanter}\right), \quad (14)$$

where  $A_{i,0}$ ,  $A_{i,1}$  and  $A_{i,2}$  are parameters obtained by regression of experimental data. The split factor  $\zeta_i$  and the molar flows of the components in the product  $(n_{i,product})$  and of the catalyst  $(n_{i,catalyst})$  as a function of the inlet flow to the decanter  $(n_{i,decanter})$  can be defined according to:

$$\zeta_i = \frac{K_i}{1 + K_i} \tag{15a}$$

$$n_{i,product} = \zeta_i n_{i,decanter} \tag{15b}$$

$$n_{i,catalyst} = (1 - \zeta_i) n_{i,decanter}.$$
 (15c)

#### C. Catalytic Mechanism

As was stated in equation (11) the reaction rate is proportional to the concentration of the active catalyst  $C_{cat}$ . Different catalyst species exist simultaneously in the reaction medium, including Rh-di-carbonyl and Rh-dimer. This phenomenon has been approximately quantified by [18] according to equation (16). The active catalyst concentration  $C_{cat}$  is expressed as a function of the Rh-precursor concentration  $C_{Rh,precursor}$ , the CO and the H<sub>2</sub> concentrations in the liquid phase. The constants  $K_1$  and  $K_2$  account for unknown reactions and the uncertainties in the catalyst pre-equilibrium.

$$C_{cat} = \frac{C_{Rh,precursor}}{1 + K_1 C_{CO} + K_2 \frac{C_{CO}}{C_{H_2}}}$$
(16)

# V. RTO PROBLEM FORMULATION

The RTO problem is formulated as the minimization of the operating costs per unit of tridecanal produced subject to the model equations and the process constraints, as expressed by:

$$\min_{\mathbf{u}} \quad \frac{Pr_{1-dodecene} \cdot F_{1-dodecene} + Pr_{Rh} \cdot F_{Rh}}{F_{tridecanal}} \quad (17a)$$

s.t. 
$$G(u) \le 0,$$
 (17b)

where  $F_i$  is the molar flow of the corresponding component ([kmol/h]) and  $Pr_i$  its price in  $\in$ /kmol. As degrees of freedom **u** the reactor temperature  $T_R$ , the decanter temperature  $T_{dec}$ , the molar fraction of carbon monoxide  $y_{CO}$ , the catalyst dosing rate  $Cat_{dos}$  and the total reactor pressure  $P_{tot}$  are considered.

TABLE II					
MODEL	vs P	LANT	PARAMETERS		

Parameter	Plant	Model I	Model II
H <sub>CO</sub> [(MPa·m <sup>3</sup> )/kmol]	910	1183	1820
$H_{H_2}$ [(MPa·m <sup>3</sup> )/kmol]	35500	46150	71000
$K_2$ [-]	1.01	0.7	2.0

TABLE III Model and Plant Optimum

		Optimum		
Process variable	Bounds	Plant	Model I	Model II
Reactor Temp. [°C]	[85-115]	85.9	85.0	88.94
Reactor Pressure [MPa]	[1.0-3.0]	3.0	3.0	3.0
CO Fraction [-]	[0.1-0.9]	0.56	0.55	0.49
Catalyst Dosing [ppm]	[0.1-5.0]	0.47	0.54	0.77
Decanter Temp. [°C]	[5-25]	5.0	5.0	5.0
cost [€/kmol]		742.24	788.27	937.98

# A. Nominal vs. (Simulated) Plant Optimum

The model and the simulated plant (henceforth it will be called plant) are described by the set of equations (11)-(17). The gas concentration in the liquid phase (i.e. the Henry coefficient, equation (12)) and the active catalyst concentration (i.e. the value of the equilibrium constant  $K_2$  in equation (16)) were identified as the variables with the largest uncertainty and two different scenarios were considered. The first scenario assumes +/-30% in parametric mismatch (Model I) while the second one considers +/-200% (Model II). The values of the uncertain parameters for the simulated plant and for the models are presented in Table II, and the comparison between the optimal values for the plant and the models is shown in Table III.

# VI. RESULTS

#### A. Performance under noise free measurements

The results obtained by applying Directional Modifier Adaptation (DMA) in the case of the first scenario using Model I are depicted in figure 4. The trajectories of the scaled inputs are displayed for 70 function evaluations. As can be observed, after less than 20 function evaluations the total pressure, the molar fraction of carbon monoxide, and the catalyst dosing are within 5% of their final value. A slower convergence is observed for the reactor temperature and the decanter temperature. After 50 function evaluations all the inputs converge to a neighborhood of their optimal values. The trajectory of the objective function is also displayed in figure 4. It can be observed that a significant reduction of the cost function is achieved after 15 iterations.

Figure 5 compares the trajectory of the objective function for different RTO schemes for the mismatch scenario with Model I. All algorithms are able to generate a sequence of inputs that converge to a neighborhood of the plant optimum. The smallest optimality lost is reached by DMA, while MAWQA converges faster to a neighborhood of the optimum. In this case the performance of the proposed scheme is between DMA and MAWQA.



Fig. 4. Trajectory of the inputs and of the cost function for 30% parametric mismatch (Model I). a) Inputs (scaled) b) Cost function



Fig. 5. Trajectory of the cost function for 30 % parametric mismatch.

A different result is observed for a larger parametric mismatch. Figure 6 displays the trajectory of the objective function when the Model II is used. In this case the largest optimality lost after 70 iterations is observed for DMA, which can be explained by the fact that the linear approximation of the sensitivities in DMA introduces a significant approximation error. The MAWQA scheme presents a slower convergence but a higher accuracy. The combination of both algorithms in the proposed scheme incorporates the advantages of both methods. A faster convergence compared to MAWQA is achieved and the final value of the objective function is closer to the actual optimum in comparison to the one obtained by DMA.

#### B. Performance under noisy measurements

Finally, the performance of the proposed method is evaluated for the case of noisy measurements. It is assumed that the



Fig. 6. Trajectory of the cost function for 200 % parametric mismatch.

 TABLE IV

 Comparison between RTO schemes under noise. Model I

	$\mathcal{N}(0,5)$		$\mathcal{N}(0, 10)$	
	ME	STD	ME	STD
DMA	20.47	7.52	28.33	13.11
MAWQA	38.75	22.47	50.96	13.48
Proposed Method	16.08	4.12	17.31	8.15

 TABLE V

 Comparison between RTO schemes under noise. Model II

	$\mathcal{N}(0,5)$		$\mathcal{N}(0, 10)$	
	ME	STD	ME	STD
DMA	43.71	8.43	46.81	17.60
MAWQA	27.63	7.37	44.27	13.89
Proposed Method	29.11	5.10	44.28	10.59

measured plant objective function  $J_{p,meas}$  is corrupted by additive Gaussian noise  $\mu$  with mean  $\mu = 0$  and variance  $\sigma^2$ .

$$J_{p,meas}^{(k)} = J_p^{(k)} + \nu^{(k)}$$
(18a)

$$p(\nu) \sim \mathcal{N}(0, \sigma^2). \tag{18b}$$

 $N_s = 10$  independent runs were performed with the stopping criterion of k = 70 functions evaluations. Two performance indicators are used. The mean error (ME) and the standard deviation (STD), calculated as :

$$ME = \sum_{j=1}^{N_s} \frac{\left|J_p^{k=70}(j) - J_p^*\right|}{N_s}, STD = \sum_{j=1}^{N_s} \frac{\left(J_p^{k=70}(j) - J_p^*\right)^2}{N_s}$$
(19)

where j is the number of the independent run and  $J_p^{k=70}$  is the final value of the objective function and  $J_p^*$  is the plant optimum.

The results of the proposed method and its comparison with DMA and MAWQA are presented in table IV for 30% parametric mismatch (Model I). Two different noise levels are considered with  $\sigma_1 = 5$  and  $\sigma_2 = 10$ . For both noise levels, the proposed methodology shows the best performance in terms of mean error and standard deviation.

If a larger parametric mismatch is considered (Model II), the performance of the proposed scheme in terms of the mean error is similar to the one yielded by the MAWQA method (see table V). However, the proposed method produces the smallest value of the standard deviation.

#### VII. CONCLUSIONS

In this work, a modifier adaptation scheme based on directional derivatives and quadratic approximation is proposed. The aim was to achieve a relatively fast convergence to the true plant optimum, despite the fact that only an inaccurate model is available. The performance of the algorithm has been illustrated by simulations for a novel chemical process and promising results were obtained. Future work involves the study of strategies for the online updating of the sensitivity matrix, as well as further studies to ensure convergence when structural plant-model mismatch is considered.

## ACKNOWLEDGMENT

This work is part of the Collaborative Research Center "Integrated Chemical Processes in Liquid Multiphase Systems"-InPROMPT. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged (TRR63)

# REFERENCES

- M. Darby, M. Nikolau, J. Jones, and D. Nicholson, "RTO: An overview and assessment of current practice," *Journal of Process Control*, vol. 21, pp. 874--884, 2011.
- [2] B. Chachuat, B. Srinivansa, and D. Bonvin, "Adaptation strategies for real-time optimization," *Computers and Chemical Engineering*, vol. 33, pp. 1557--1567, 2009.
- [3] W. Gao and S. Engell, "Iterative set-point optimization of batch chromatography," *Computers and Chemical Engineering*, vol. 29, pp. 1401--1409, 2005.
- [4] P. Tatjewski, "Iterative optimizing set-point control- the basic principle redesigned," in *15th Triennal World Congress IFAC*, 2002.
- [5] A. Marchetti, B. Chachuat, and D. Bonvin, "Modifier-adaptation methodology for real-time optimization," *Ind. Eng. Chem. Res.*, vol. 48, pp. 6022--6033, 2009.
- [6] P. Roberts, "An algorithm for steady-state system optimization and parameter-estimation," *International Journal of Systems Science*, vol. 10, pp. 719--734, 1979.
- [7] A. Marchetti, B. Chachuat, and D. Bonvin, "A dual modifier-adaptation approach for real-time optimization," *Journal of Process Control*, vol. 20, pp. 1027--1037, 2010.
- [8] D. Navia, L. Briceno, G. Gutierrez, and C. de Prada, "Modifieradaptation methodology for real-time optimization reformulated as a nested optimization problem," *Ind. and Chem. Eng. Res.*, vol. 48, no. 54, pp. 12 054-12 071, 2015.
- [9] W. Gao, S. Wenzel, and S. Engell, "A reliable modifier-adaptation strategy for real-time optimization," *Computers and Chemical Engineering*, vol. 91, pp. 318--328, 2016.
- [10] S. Costello, G. Francois, and D. Bonvin, "A directonal modifieradaptation algorithm for real-time optimization," *Journal of Process Control*, vol. 39, pp. 64--76, 2016.
- [11] G. A. Bunin, "On the equivalence between the modifier-adaptation and trust-region frameworks," *Computers and Chemical Engineering*, vol. 71, pp. 154--157, 2014.
- [12] Y. Brunsch and A. Behr, "Temperature controlled catalyst recycling in homogeneous transition-metal catalyst: minimization of catalyst leaching," Ang. Chem. Int. Ed, vol. 52, pp. 1586--1589, 2013.
- [13] J. Dreimann, P. Lutze, M. Zagajewski, A. Behr, A. Gorak, and A. Vorholt, "Highly integrated reactor-separator systems for the recycling of homogeneous catalysis," *Chemical Engineering and Processing: Process Intensification*, vol. 99, pp. 124–131, 2016.
- [14] M. Zagajewski, A. Behr, P. Sasse, and J. Wittman, "Continuously operated miniplant for the rhodium catalyzed hydroformylation of 1dodecene in a thermomorphic multicomponent solvent system (tms)," *Chemical Engineering Science*, vol. 115, pp. 88--94, 2014.
- [15] C. Netwich and S. Engell, "Application of surrogate models for the optimization and design of chemical processes," in *International Join Conference on Neural Network (IJCNN) 2016*, 2017.
  [16] R. Hernandez and S. Engell, "Modelling and iterative real-time opti-
- [16] R. Hernandez and S. Engell, "Modelling and iterative real-time optimization of a homogeneously catalyzed hydroformylation process," in *Computer Aided Chemical Engineering*, vol. 38, 2016, pp. 1--6.
- [17] G. Kiedorf, D. Hoang, A. Mueller, A. Joerke, J. Markert, H. Arellano-Garcia, A. Siedel-Morgenstern, and C. Hamel, "Kinetics of 1-dodecene hydroformylation in a thermomorphic solvent system using rhodium-biphephos catalyst," *Chemical Engineering Science*, vol. 115, pp. 31--48, 2014.
- [18] B. Hentschel, G. Kiedrof, M. Gerlach, C. Hamel, A. Siedel-Morgenstern, H. Freund, and K. Sundmacher, "Model-based identification and experimental validation of the optimal reaction route for the hydroformylation of 1- dodecene," *Industrial and Engineering Chemistry Research*, vol. 54, pp. 1755--1765, 2015.