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MOVING HORIZON ESTIMATION AND OPTIMAL EXCITATION IN TEMPERATURE OSCILLATION CALORIMETRY

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Abstract: Calorimetry is a frequently used tool for monitoring and control of chemical reactors. In the case of laboratory-scale reactors with small temperature gradients in the jacket, an additional excitation has to be introduced in order to get reliable estimates if both heat of reaction and heat transfer coefficient are estimated. This is usually referred to as *temperature oscillation calorimetry (TOC)*. In this paper, we introduce a moving horizon estimator that evaluates the data obtained by TOC in real time. In contrast to conventional TOC, this approach is not restricted to sinusoidal signals. Thus the question which excitation yields the best estimates is natural here. The standard deviation of the estimate is taken as a reliability measure.

Keywords: oscillation calorimetry, moving horizon estimation, optimal excitation

1. INTRODUCTION

For the production of chemicals in batch or semi-batch reactors, the knowledge of the concentrations of the reactants is extremely important for monitoring and control purposes. Instead of directly measuring them (e.g. by Raman spectroscopy), which can be a laborious and costly task, *calorimetry* provides a good and reliable altexrnative for exothermic reactions (Elizalde *et al.*, 2005). In calorimetry, several temperature measurements (reactor temperature T_R, jacket temperature T_J and jacket inlet temperature $T_{J,in}$) are used for the estimation of the produced heat of reaction $\dot{Q}_R$, which in turn can be used for the estimation of the current concentrations in the reactor. If the heat transfer coefficient kA is either unknown or changes during the reaction, both quantities can be estimated using the heat balances of the reactor and the jacket. In the case of batch reactors these equations read:

$$\frac{dT_R}{dt} = \frac{\dot{Q}_R}{m_R\, c_p} - \frac{kA}{m_R\, c_p}(T_R - T_J) \quad (1)$$

$$\frac{dT_J}{dt} = \frac{kA}{m_J c_p}\,(T_R - T_J) + \frac{\dot{m}}{m_J}\,(T_{J,in} - T_J)\,. \quad (2)$$

Calorimetry is a wide-spread technique in industrial applications. However, when it comes to laboratory and pilot plant reactors, the coolant flowrate through the jacket, $\dot{m}$, is usually set extremely high such that a uniform temperature in the jacket can be achieved (Buruaga *et al.*, 1997). Thus the resulting temperature difference of the inlet and outlet temperatures of the jacket $(T_{J,in} - T_J)$ cannot be measured reliably any more. If the temperature measurements carry only white noise with zero mean, a suitable filter might help to overcome this problem. However, already a slight offset in the measurements leads to a strongly amplified offset in the estimation of kA.

A solution to this problem was proposed by (Carloff *et al.*, 1994) and later improved by (Tietze *et al.*, 1996). The idea is to excite the dynamics of the system by adding a sinusoidal signal to the temperature trajectories. This can be done either by using a heating device inside the reactor or by varying the jacket inlet temperature. According to (Tietze *et al.*, 1996), kA can be computed from the ratio of the amplitudes of the reactor temperature oscillation and the jacket temperature oscillation, δT_R and δT_J as

$$\begin{aligned} kA &= \frac{m_R\, c_p\, \omega}{\tan\left(\arccos\left[\frac{\delta T_R}{\delta T_J}\right]\right)} \\ &= \frac{m_R\, c_p\, \omega}{\sqrt{1-\left(\frac{\delta T_R}{\delta T_J}\right)^2}} \frac{\delta T_R}{\delta T_J}. \end{aligned} \tag{3}$$

Once kA is known, the heat of reaction can be estimated from Eq. (1). As the formulas exhibit, the jacket inlet temperature measurement $T_{J,in}$, thus the problem mentioned above does not occur. Although this strategy has been proven to work reasonably well, it has some drawbacks. The computation of the amplitudes requires 1.5 periods of data where the temperatures are assumed to be perfectly sinusoidally shaped. First, this yields a delay of the estimate of 1 period. The oscillation period can however not be chosen too short because the attenuation of the T_R signal is too high at high frequencies. Secondly, if a disturbance (such as the start of the reaction) is introduced into the system, a period of several system time constants $\left(T = \frac{m_R c_p}{kA}\right)$ is required to return to a (cyclic) steady state and thus to produce more or less perfect sine signals again. During the transient phase, the estimates are highly unreliable.

In Section 2 of this paper, an alternative algorithm for the estimation of kA and $\dot{Q}_R$ which does not rely on the sinusoidal shape of the signal is introduced. Chapter 3 tackles the question whether or not a sinusoidal signal is the optimal excitation for the system and which signal provides maximum information to the estimator. Finally, some conclusions are drawn.

2. MOVING HORIZON ESTIMATION

It can be shown quite easily that the two quantities kA and $\dot{Q}_R$ are not linearly observable if only Eq. (1) is used to describe the reactor. Thus, a strategy that is based on parameter estimation has to be used in the case of reactors with high jacket flowrates.

One possibility is the *moving horizon estimator* (MHE) (Rao *et al.*, 2001; Diehl *et al.*, 2006*b*). In the approach used here, not only the difference between the measured and estimated reactor temperature but also the difference between the measured and estimated jacket temperature contributes to the cost function. No weights for the different entries are used as both temperatures are assumed to contain similar measurement errors. The reactor energy balance (Eq. (1)) is discretized using finite central differences. If all reactor temperature measurements in the horizon considered $T_{R,k-n} \dots T_{R,k}$ are collected in the vector $\mathbf{r} \in \Re^{n+1}$ and all jacket temperature measurements of importance $T_{J,k-n+1} \dots T_{J,k-1}$ are collected in the vector $\mathbf{j} \in \Re^{n-1}$, this leads to the following formulation of the MHE problem:

$$\min_{p_1,p_2,\hat{\mathbf{r}},\hat{\mathbf{j}}} \left((\mathbf{r}-\hat{\mathbf{r}})^T(\mathbf{r}-\hat{\mathbf{r}}) + (\mathbf{j}-\hat{\mathbf{j}})^T(\mathbf{j}-\hat{\mathbf{j}})\right) \tag{4}$$

$$\begin{aligned} \text{s.t.} \qquad \mathbf{0} &= \mathbf{M}_{\text{fut}}\hat{\mathbf{r}} - \mathbf{M}_{\text{past}}\hat{\mathbf{r}} - 2p_1\mathbf{e}_n \\ &\quad +2\, p_2 \left(\mathbf{M}_{\text{cur}}\hat{\mathbf{r}} - \hat{\mathbf{j}}\right) \end{aligned} \tag{5}$$

$$\mathbf{M}_{\text{fut}} = \begin{pmatrix} 0 & 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 0 & 1 & \dots & 0 \\ & & & & & \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{r} = \begin{pmatrix} T_{R,k-n} \\ \vdots \\ T_{R,k} \end{pmatrix}$$

$$\mathbf{M}_{\text{cur}} = \begin{pmatrix} 0 & 1 & 0 & 0 & \dots & 0 \\ 0 & 0 & 1 & 0 & \dots & 0 \\ & & & & & \\ 0 & 0 & \vdots & \ddots & \vdots & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \qquad \mathbf{j} = \begin{pmatrix} T_{J,k-n+1} \\ \vdots \\ T_{J,k-1} \end{pmatrix}$$

$$\mathbf{M}_{\text{past}} = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 & 0 \\ 0 & 1 & 0 & \dots & 0 & 0 \\ & & & & & \\ 0 & \vdots & \ddots & \vdots & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$p_1 = \frac{h}{m\, c_p}\dot{Q}_R \qquad ; \qquad p_2 = \frac{h}{m\, c_p} kA.$$

It can be seen that (4) is a high dimensional optimization problem as the vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{j}}$ are estimated together with the system parameters p_1 and p_2 (which are proportional to $\dot{Q}_R$ and kA, respectively). Instead of a direct numerical solution we derived a semi analytical solution to this problem. This solution satisfies equations of the form:

$$\begin{aligned} [p_1, \hat{\mathbf{r}}, \hat{\mathbf{j}}] &= \tilde{\mathbf{f}}(p_2) && (Eq.(6)-(8)) \\ \tilde{f}(p_1, p_2, \hat{\mathbf{r}}, \hat{\mathbf{j}}) &= \quad 0 && (Eq.(9)). \end{aligned}$$

Thus the problem can be reduced to a one dimensional root finding problem. The precise equations read:

$$\begin{aligned} \mathbf{M}^* &= \mathbf{M}_{\text{fut}} - \mathbf{M}_{\text{past}} + 2p_2\mathbf{M}_{\text{cur}} \\ \hat{\mathbf{j}} &= \left(2p_2\, \mathbf{I} + \frac{1}{p_2}\mathbf{M}^*\, \mathbf{M}^{*T}\right)^{-1} \\ &\quad \cdot \left(-2p_1\mathbf{e}_n + \mathbf{M}^*\, \mathbf{r} + \frac{1}{p_2}\mathbf{M}^*\, \mathbf{M}^{*T}\, \mathbf{j}\right) \end{aligned} \tag{6}$$

$$\begin{aligned}
\mathbf{a} &= -\frac{1}{p_2}\left(\mathbf{j}-\hat{\mathbf{j}}\right)\\
\hat{\mathbf{r}} &= \mathbf{r}-\frac{1}{2}\mathbf{M}^{*T}\mathbf{a} \qquad (7)\\
\tilde{\mathbf{h}} &= \left(2p_2\,\mathbf{I}+\frac{1}{p_2}\mathbf{M}^*\,\mathbf{M}^{*T}\right)^{-1}\\
&\quad\cdot\left(\mathbf{M}^*\,\mathbf{r}+\frac{1}{p_2}\mathbf{M}^*\,\mathbf{M}^{*T}\,\mathbf{j}\right)\\
p_1 &= -\frac{\mathbf{e}_n\left(\mathbf{j}-\tilde{\mathbf{h}}\right)}{\mathbf{e}_n\left(2p_2\,\mathbf{I}+\frac{1}{p_2}\mathbf{M}^*\,\mathbf{M}^{*T}\right)^{-1}\mathbf{e}_n} \qquad (8)
\end{aligned}$$

$$0 = \mathbf{a}^T(\mathbf{M}_{\text{past}}\hat{\mathbf{r}}-\hat{\mathbf{j}}). \qquad (9)$$

This scheme can be implemented by applying a root finding strategy for p_2 to Eq. (9). Each evaluation of Eq. (9) requires the evaluation of (6) - (8) which in turn requires one inversion of the matrix $\left(2p_2\,\mathbf{I}+\frac{1}{p_2}\mathbf{M}^*\,\mathbf{M}^{*T}\right)$. For a reasonable number of measurements (e.g. 66 as used in the validation example), this formulation of the MHE can be used in online applications.

2.1 Performance of the MHE

In order to validate the performance of the MHE, it was applied to several data sets. For the sake of brevity, only one representative result is shown in Figure 1. In this experiment, a jacket cooled $1l$ glass reactor equipped with a PI controller for the reactor temperature T_R was heated by an electrical heating rod with variable power levels. In order to realize the oscillations, a sine signal was added to the T_R setpoint as shown in Figure 1 (top). During the experiment, the heating rod was set to five different power levels.

For real applications, the MHE as well as the classical approach (3) require two parameters: The heat capacity of the reactor contents ($m\ c_p$) and the heat loss to the environment, which is modeled here as

$$\dot{Q}_{loss} = (kA)_{env}\,(T_R - T_{env}). \qquad (10)$$

The MHE was implemented with 66 measurements in the horizon. The free parameters were adjusted such that $\dot{Q}_R$ is equal to the known values at $t = 0.5h$ and $t = 3.5h$.
It can be seen that the estimates of the MHE contain slight oscillations. This is due to the use of a discretization (5) instead of the continuous model (1). However, the MHE exhibits a much faster convergence than the classical approach (3). This can mainly be explained by the fact that in (3) - in contrast to the MHE - a perfect sinusoidal signal for the 1.5 periods prior to the point where the estimation takes place is assumed. This condition is however not fulfilled after every step of $\dot{Q}_R$ as T_R needs time for reaching its new (cyclic) steady state. This transition lasts for several system time constants. The slight delay in the MHE estimate originates from the assumption that $\dot{Q}_R$ is constant within its horizon which was chosen as half a period in this example.

3. OPTIMAL EXCITATION

Classical oscillation calorimetry uses a sinusoidal signal to overcome the "loss" of Eq. (2) in small reactors. This choice is due to the fact that is enables a straightforward computation of the desired parameters from the resulting amplitudes in the system (Eq. (3)).
The sine wave is introduced to excite the system and to obtain additional information in the data which is not available at steady state. As the MHE is not restricted to a sinusoidal input signal, the question arises which input signal ($T_{J,in}$) yields most information for the estimator.
In order to answer this question, the framework of nonlinear optimal experimental design, which has been explained e.g. in (Körkel *et al.*, 2004), is used. The idea is to minimize the covariances of the estimates (normalized by the error variances which are assumed here to be equal for all measurements). For general nonlinear problems, the determination of this normalized covariance matrix is rather difficult, however for the linearization of Eqs. (4) - (5), a closed form can be obtained which is equivalent to a sensitivity analysis of the error covariance. Here, $\mathbf{p} = [p_1, p_2, \hat{\mathbf{r}}^T, \hat{\mathbf{j}}^T]^T$ represents the full set of parameters to be estimated and $\Delta\mathbf{p}$ represents its deviation from the estimated value. If instead of the central differences discretization in Eq. (5) a forward differences approach is used, the normalized covariance $\mathbf{C}$ can be computed from

$$\begin{aligned}
\mathbf{C}(\Delta\mathbf{p}) &= E(\Delta\mathbf{p}\Delta\mathbf{p}^T)\\
&= \mathbf{J}^+\begin{pmatrix}\mathbf{I} & \mathbf{0}\\ \mathbf{0} & \mathbf{0}\end{pmatrix}\mathbf{J}^{+^T} \qquad (11)\\
\text{with}\quad \mathbf{J}^+ &= (\mathbf{I}\quad \mathbf{0})\begin{pmatrix}\mathbf{J}_1^T\mathbf{J}_1 & \mathbf{J}_2^T\\ \mathbf{J}_2 & \mathbf{0}\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{J}_1^T & \mathbf{0}\\ \mathbf{0} & \mathbf{I}\end{pmatrix}\\
\mathbf{J}_1 &= \begin{pmatrix}0&0&-1&0&\cdots&0\\0&0&0&-1&\cdots&0\\ \vdots&\vdots&0&0&\ddots&0\\0&0&0&0&\cdots&-1\end{pmatrix}\\
\mathbf{J}_2 &= \begin{bmatrix}-\mathbf{e}_n^T\\ (\tilde{\mathbf{M}}_{past}\hat{\mathbf{r}}-\hat{\mathbf{j}})^T\\ (\tilde{\mathbf{M}}_{fut}-(1-p_2)\tilde{\mathbf{M}}_{past})^T\\ (-p_2\,\mathbf{I})\end{bmatrix}^T.
\end{aligned}$$

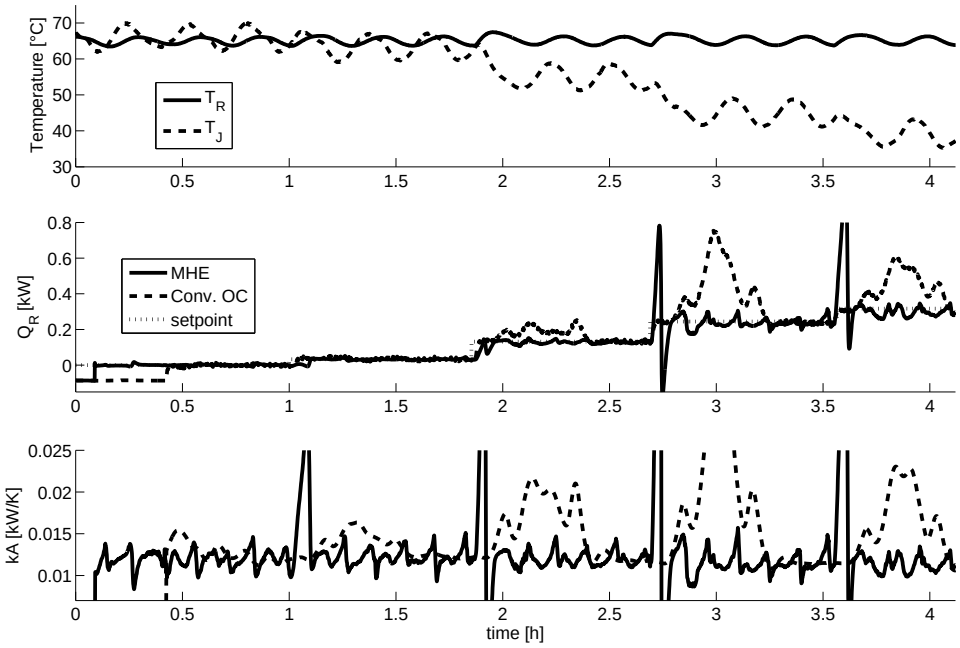


Fig. 1. Application of the MHE and conventional oscillation calorimetry to an experiment performed in a 1 l glass reactor

The complete normalized covariance matrix $\mathbf{C}$ is not of interest as it also contains the normalized covariances of the estimated temperature vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{j}}$. In order to judge the quality of the estimate, only the important covariances of the $\dot{Q}_R$ estimate ($C_{1,1}$) and the kA estimate ($C_{2,2}$) are extracted and combined using a modified version of the so-called *A criterion*

$$\phi(\mathbf{C}) = \frac{\sqrt{C_{1,1}}}{p_1^*} + \frac{\sqrt{C_{2,2}}}{p_2^*}, \tag{12}$$

where p_1^* and p_2^* represent characteristic scales. In case the true values are known, those can be used here ($p_1^* = p_1;\ p_2^* = p_2$).
Using a control vector parameterization, the resulting optimization problem can be written as

$$\min_{\mathbf{T_{J,in}}} \quad \phi(\mathbf{C}) \tag{13}$$

$$s.t. \qquad \frac{d\,[\hat{\mathbf{r}},\hat{\mathbf{j}}]^T}{dt} = \mathbf{f}(T_{R,0}, T_{J,0}, \mathbf{T_{J,in}}, \tilde{\mathbf{p}}) \tag{14}$$

$$0 \leq \mathbf{g}(\hat{\mathbf{r}}, \mathbf{T_{J,in}}). \tag{15}$$

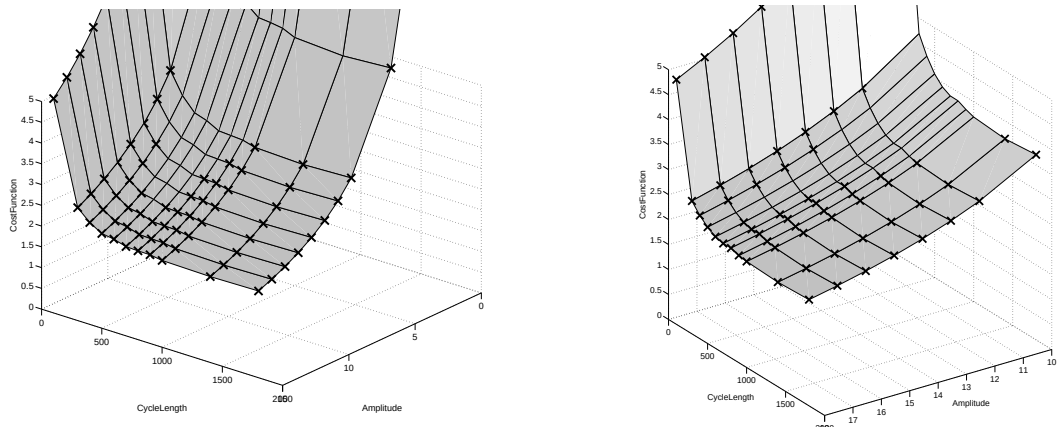
$\mathbf{T_{J,in}}$ is the vector of jacket inlet temperatures and $\tilde{\mathbf{p}} = [\dot{Q}_R, kA, m_R, m_J, \dot{m}_J, c_p]$ is the vector of parameters required for the simulation of the system. The function $\mathbf{g}$ in Eq. (15) represents inequality constraints which restrict the amplitude of the reactor temperature $\mathbf{r}$ and the maximal slope of the jacket inlet temperature trajectory $\mathbf{T_{J,in}}$.
This computation is performed for the linearization around the nominal "true" measurements which are obtained from a simulation of the model $\mathbf{f}$ (Eqs. (1) - (2)). As the measurement noise is assumed to be a zero mean process, it does not appear explicitly in the computations.

3.1 Implementation

Numerical studies have shown that the difficulty to estimate $\dot{Q}_R$ and kA increases with increasing $\dot{Q}_R$. Therefore the optimization was performed in a (simulated) 10 l metal reactor, similar to the one used in the Process Control Laboratory, with a heat of reaction of $\dot{Q}_R = 1\ kW$. The kA value was chosen to be $kA = 0.3$. As characteristic scales, $p_2^* = \frac{kA}{m\ c_p}h = 0.00357$ and $p_1^* = \frac{\dot{Q}_R}{m\ c_p}h = 0.12$ were chosen. The initial temperatures are $T_{J,0} = 60\ ^oC$ and $T_{R,0} = 76.7\ ^oC$ which correspond to the steady state values. The reactor temperature was restricted to $75.7\ ^oC < T_R < 77.7\ ^oC$ and the jacket inlet temperature to $30\ ^oC < T_{J,in} < 90\ ^oC$. The maximum slope of the jacket temperature trajectory was constrained to $\left|\frac{dT_{J,in}}{dt}\right|_{max} = 0.14\ \frac{^oC}{s}$. One hour of experiment was considered.

3.2 Numerical results

In a first attempt, $\mathbf{T_{J,in}}$ was discretized with 20 equidistant points and interpolated linearly. The covariance was computed from temperature data sampled every $h = 30s$. The optimization problem can be solved on a standard PC.
In order to avoid a locally optimal solution, the problem was initialized from different initial guesses including a flat profile, different sinusoidal



(a) Sine (b) ZigZag

Fig. 3. The behavior of the cost function (Eq. (12)) with two independent parameters (amplitude, frequency). The crossed points ($\mathbf{x}$) are points that violate the constraints.

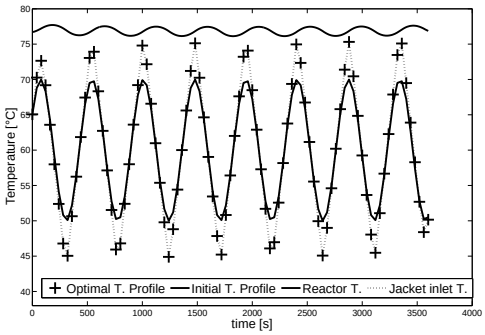


Fig. 2. Result of the optimization with 90 discretization points

profiles and different zigzag profiles. The solutions, which are omitted here for the sake of brevity, show clearly that the optimizer tries to introduce as much variation as possible by hitting the constraints as often as possible. However, due to the small number of discretization points, it cannot be determined clearly whether a sine wave or a zigzag profile is advantageous.

Therefore, another optimization using a parameterization of $\mathbf{T_{J,in}}$ by 90 points was performed using the best sinusoidal solution obtained before as initial value. This time, the temperature data was sampled every $h = 5s$. The result is depicted in Figure 2. It can be seen that, although initialized with a sinusoidal profile, the optimizer converges to a zigzag profile. The explanation is that if the maximal slope is restricted, the sinusoidal profile has a smaller amplitude compared to the zigzag profile which leads to a lower amplitude of the reactor temperature T_R and thus to less dynamics in the system. In order to quantify the advantage of the zigzag profile over the sine profile, a different discretization was chosen: Both profiles can be characterized by an amplitude and a cycle time.

With this discretization two more optimizations were performed. The results are shown in Table 1. In order to ensure global optimality, the plot of $\phi(\mathbf{C})$ versus amplitude and frequency is shown in Figure 3. The crosses denote points that violate the constraints.

Signal profile	*Cycle Time*	*Amplitude*	$\phi(\mathbf{C})$
Sine	581.3	13.01	2.52
Zigzag	510	17.8	2.34

Table 1. The result of the optimization with only 2 degrees of freedom

It can be seen that the zigzag profile reduces the standard deviation by approx. 8 % compared to the sinusoidal excitation.

4. CONCLUSIONS

When small batch reactors are considered, the jacket flowrate is usually so high that the jacket inlet temperature is close to to the jacket outlet temperature. This makes the evaluation of the jacket heat balance (Eq. (2)) practically impossible and leads to the need of introduction of an additional excitation of the system. This enables a nonlinear estimation of the heat transfer coefficient kA and the heat of reaction $\dot{Q}_R$ from the reactor heat balance (Eq. (1)).

In this contribution, a moving horizon estimator and a semi analytical solution of the optimization problem has been proposed. Its superior performance compared to conventional temperature oscillation calorimetry is demonstrated.

As the MHE is not based on the assumption of sinusoidal oscillations of the different temperatures involved, the question which signal gives the optimal excitation for the parameter estimation was posed. It turned out that the sinusoidal signal

is slightly suboptimal and that a zigzag signal yields an improvement of about 8 % in terms of the standard deviations of the estimates if the slope of the excitation signal is constrained.

In order to improve the performance of the MHE further, two more issues will be investigated in the future. First, the finite differences discretization (Eq. (5)) of the reactor heat balance (Eq. (1)), which leads to oscillations in the estimate, can be replaced by its analytical solution assuming a first order hold of the jacket temperature. Secondly, an additional regularization term (e.g. $(\|p_1 - p_{1,\text{old}}\| + \|p_2 - p_{2,\text{old}}\|)$) as proposed by (Rao *et al.*, 2001) and (Diehl *et al.*, 2006*a*) can be introduced into the cost function in order to account for knowledge from past periods. The financial support from the Deutsche Forschungsgemeinschaft DFG (grant EN 152/31-3) is gratefully appreciated.

5. LIST OF SYMBOLS

5.1 Latin symbols

Symbol	*Explanation*	*Unit*
$\mathbf{C}$	Normalized covariance matrix	*mixed*
$\mathbf{e}_n$	Unit vector $[1\ 1\ \cdots\ 1]^T \in \Re^n$	[−]
$\mathbf{j}$	Vector of jacket temperatures	^oC
Q	Energy	kJ
$\mathbf{r}$	Vector of reactor temperatures	^oC
T	Temperature	^oC
c_p	Heat capacity	$\frac{kJ}{kg\ K}$
$\mathbf{f}$	Model (Eqs. (1) - (2))	
$\tilde{\mathbf{f}}$	Solution equations of the optimization problem (Eqs. (6) - (8))	
$\mathbf{g}$	Inequality constraints	
h	Sampling time	s
kA	Heat transfer coefficient	$\frac{kJ}{K}$
m	Mass	kg
n	Dimension of $\mathbf{j}$ (number of considered measurements)	[-]
$\mathbf{p}$	Vector of all parameters to be identified	*mixed*
$\tilde{\mathbf{p}}$	Vector of parameters that determine the simulation of the reactor and the jacket	*mixed*

5.2 Greek symbols

Symbol	*Explanation*
δ	Amplitude
ω	Frequency
ϕ	Cost function (weighted standard deviation)

5.3 Sub-/Superscripts

Symbol	*Explanation*
$_R$	Reactor
$_J$	Jacket
$_{J,in}$	Jacket inlet
$\dot{}$	Time derivative
$\hat{}$	Estimated state
*	Characteristic value

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