ONLINE MONITORING OF SEMI-CONTINUOUS EMULSION COPOLYMERIZATION: COMPARING CONSTRAINED EXTENDED KALMAN FILTERING TO FEED-FORWARD CALORIMETRY

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Abstract: Semi-continuous emulsion copolymerization (SCEP) is one of the major processes for the production of polymer latexes. For tailor-made copolymers, SCEP is employed because better control of polymer quality is possible compared to batch operation. To efficiently produce high quality polymers, recipe optimization and good feedback process control is required. For optimization or control purposes it is necessary to measure important product qualities such as the composition of the copolymer or the average chain length of the macromolecules. Measurements of these properties for this multi-phase process are expensive and usually not available online. State estimation and reaction calorimetry are possibilities to overcome this problem. Starting from a complex model for the considered process we develop a simplified model which enables us to estimate the concentrations of the monomers in the particle phase and thus the composition of the copolymer using a Constrained Extended Kalman Filter (CEKF). We compare this to earlier approaches based on simple feed-forward calorimetry and show that it is more robust to modelling errors and to the choice of initial value. *Copyright © 2001 IFAC*

Keywords: state estimation, emulsion polymerization, calorimetry, nonlinear systems

1. INTRODUCTION

1.1 *General*

Semi-continuous emulsion polymerization (SCEP) is a very versatile polymerization technique for making polymer latexes, applicable to many monomer types in batch, semi-batch and continuous processes. Its products are used as paints, adhesives, coatings and binders.

Due to the multiphase and compartmentalized nature of the process, polymers with unique properties and a small width of chain length distribution can be prepared, and the heat is removed fast and efficiently.

Software sensors are often applied to SCEP processes as important product qualities are not measureable online. Quality measurements are necessary for control or optimization purposes.

In SCEP, the product quality is determined by the stochastic distribution of the different monomers in the polymer chain. As the reaction rates of the monomers, in our case Vinylacetate (A or 1) and Butylacrylate (B or 2), differ extremely, this goal cannot be achieved without control if short batch times are to be realized. Without control, the process has to be run under starved conditions where the feed rate is always considerably smaller than the slowest reaction rate. For composition control it is necessary to measure the concentrations of the monomers in the particle phase, as the particles are the main reaction loci. This concentration cannot be measured online.

1.2 Earlier research

In (Dimitratos, 1989) the measurement of the reactor concentration of the monomers was realized by gas chromatography, subject to a time delay larger than 10 minutes, which poses problems for on-line control. From these measurements, an EKF estimates the particle phase concentrations.

Reaction calorimetry, on the other hand, is a well established technique for on-line measurement of reaction rates. The measurement is noninvasive, rapid, and robust, being based only on temperature and flow measurements.

(Urretabizkaia et al., 1993) and (Gugliotta et al., 1995) developed a calorimetry based approach to estimate conversion and copolymer composition in emulsion copolymerization systems. Rather than giving direct measurements of either the rate of polymerization or of the polymer composition, the heat of reaction is calculated by calorimetry and used as a parameter in the reaction term of the monomer material balances. The material balances are integrated without feedback using this additional information. This approach (from now on simply called calorimetry) produces good results for precisely known initial conditions and the absence of disturbances.

However, as feed-forward approaches as a rule cannot reject disturbances and are sensitive to plant-model mismatch, state estimation based on calorimetric data seems to be an alternative to the mentioned approaches.

1.3 Research in this paper

We consider an SCEP-process which is run in a pilot plant. Because the reactor is not constructed as a calorimeter, heat balances for the cooling jacket and reactor medium are used in the model. We first give an overview about the general model which is based on (Dimitratos, 1989; Urretabizkaia et al., 1994). Because of the bad observability properties of the full model the model is simplified. The resulting model is of third order and describes the reaction temperature and the concentrations of butylacrylate and vinylacetate in the particle phase. Based on this simplified model a Constrained Extended Kalman Filter is designed and is compared with results from calorimetry.

We investigate the differences of the two approaches for both parameter uncertainties and initial condition errors and show that the CEKF still gives good results when the calorimetry cannot estimate the process states correctly.

2. MODEL OF THE SCEP

The process model consists of six differential equations and one algebraic equation to determine the average number of radicals per particle $\bar{n}$ and is based on the following assumptions:

- there is no reaction in the water phase;
- the number of particle is assumed to be constant;
- there is no gel effect.

2.1 Phase distribution

The monomers are distributed in all three phases of the system. To determine the concentrations of the monomers in the phases, the phase distribution algorithm used by (Urretabizkaia and Asua, 1994) is used. It employs constant phase partition coefficients for the equilibrium between the phases K_i^j, where i defines the considered monomer, j the phase (P-Particle, M-Droplet). The phase distribution algorithm calculates the volumes of the monomers in the phases and the total volume of each monomer in the reactor. The interested reader is referred to (Urretabizkaia and Asua, 1994) for a detailed description of the algorithm. This approach gives good results and converges quickly.

2.2 Reaction model and heat balances

The dynamic model is determined by mass and heat balances. The mass balances for the monomers are:

$$\frac{d[i]^R}{dt} = \frac{1}{V^R}\left(-R_i - \frac{dV^R}{dt}[i]^R + \dot{n}_i\right) \quad (1)$$

with
$$R_i = \sum_{j=1}^{n} k_{Pij}P_j[i]\frac{\bar{n}N_T}{N_A} \quad i \in [A,B]$$

$$P_A = \frac{k_{BA}[A]^P}{k_{BA}[A]^P + k_{AB}[B]^P}$$

$$P_B = 1 - P_A. \quad (2)$$

The reaction rate constants are assumed to be temperature dependent:

$$k(T) = k_{\infty}\exp\left(-\frac{E_A}{R_0}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right). \quad (3)$$

The parameters k_{∞} and E_A were calculated from literature data (Dimitratos, 1989; Urretabizkaia and Asua, 1994) by regression.

Ignoring the gel effect and radical desorption, Smith and Ewart (Smith and Ewart, 1948) derived the following equation for the average number of radicals per particle $\bar{n}$:

$$\bar{n} = \frac{N_A}{N_T}\sqrt{\frac{R_I V^P V^R}{2\bar{k}_t}}. \quad (4)$$

As R_I depends on the concentration of the initiator, the concerning dynamic equation has to be considered.

$$\frac{d[I]^R}{dt} = R_I = \frac{1}{V^R}\left(-2fk_d[I]^R - \frac{dV^R}{dt}[I]^R\right). \quad (5)$$

The time dependence of the volume is determined by the monomer feed $\dot{n}_A$, $\dot{n}_B$ and the volume contraction by reaction:
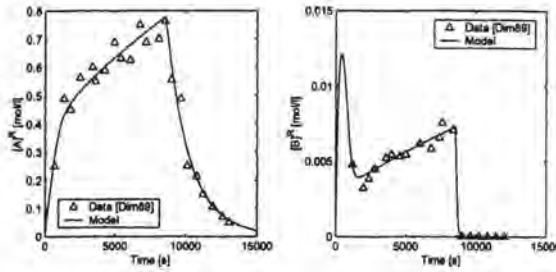
Fig. 1. Reactor concentration of monomer A and B

$$\frac{dV^R}{dt} = \sum_i \dot{n}_i \bar{V}_i + \sum_i R_i M_i \left(\frac{1}{\rho_{Pol}} - \frac{1}{\rho_i} \right). \quad (6)$$

Finally dynamic equations for the temperatures in the reactor and the jacket were derived:

$$\frac{dT_R}{dt} = \frac{1}{C_S} \left(\sum_{i=1}^{2} R_i(-\Delta H_i) + \sum_{i=1}^{2} \dot{n}_i M_i c_{p_i} \right.$$
$$\left. \times (T_{Rin} - T_R) + kA(T_J - T_R) \right) \quad (7)$$

$$\frac{dT_J}{dt} = \frac{1}{C_J} \left(\dot{m}_{Oel} c_{p_{Oel}}(T_{Jin} - T_J) \right.$$
$$\left. - kA(T_J - T_R) \right). \quad (8)$$

C_J decribes the combined heat capacity of the liquid in the jacket. The heat capacity of the liquid in the reactor and the reactor, C_S, and the heat transfer area A are algebraic functions of the liquid volume in the reactor. As shown in figure 1 this model fits experimental data from literature (Dimitratos, 1989) well. The full model is used to generate sampled process data, and the concentrations of the full model are compared with the estimations by the CEKF and the calorimetry. The simulated temperatures are passed to the estimation as measurements.

3. CALORIMETRY

Following (Gugliotta *et al.*, 1995) and combining the equations (7) and (8), the overall heat of reaction is calculated as follows:

$$\dot{Q}_R = C_R \frac{dT_R}{dt} - \sum_{i=1}^{2} c_{p_i} \dot{n}_i M_i (T_{Rin} - T_R)$$
$$+ \frac{dT_J}{dt} c_{PCM} m_{CM} - \dot{m}_{CM} c_{p_{Oel}} (T_{Jin} - T_J). \quad (9)$$

$\frac{dT_R}{dt}$ and $\frac{dT_J}{dt}$ are estimated using a backwards difference method.
The heat of reaction is given as

$$\dot{Q}_R = \sum_{i=1}^{2} R_i(-\Delta H_i). \quad (10)$$

Using equation (2), in equation (10) $\frac{\bar{n} N_T}{N_A}$ (the amount of radicals in *mol*) can be calculated:

$$\frac{\bar{n} N_T}{N_A} = \frac{-\dot{Q}_R}{\sum_{i=1}^{n} \sum_{j=1}^{n} k_{ji} P_j [i]^P \Delta H_i}. \quad (11)$$

The product on the right hand side of equation (11) is used as a parameter in the material and volume balances (eqns. 1 and 6). When the model is integrated, equation (4) is not necessary as $\frac{\bar{n} N_T}{N_A}$ is computed directly from calorimetry.

4. MODEL REDUCTION

For control purposes it is necessary to know the concentrations of the monomers in the particle phase as they determine the reaction rate and thus the composition of the polymer. The dynamic equations (1) depend on the concentrations in the reactor as well as on the concentrations in the particle phase. In order to derive differential equations for the monomer concentrations in the particle phase, it is assumed that no droplet phase occurs. Using

$$[i]^R V^R = \left(V^P + \frac{V^W}{K_i^P} \right) [i]^P \quad (12)$$

the concentration of monomer i in the particle phase can be described by

$$\frac{d[i]^P}{dt} = \frac{1}{\left(V^P + \frac{V^W}{K_i^P} \right)} \left(\dot{n}_i - R_i \right. \quad (13)$$
$$\left. -[i]^P \left(\frac{dV^P}{dt} \left(1 - \frac{1}{K_i^P} \right) + \frac{1}{K_i^P} \frac{dV^R}{dt} \right) \right).$$

The volume of the particle phase is also time dependent. If an equilibrium of the phase distribution is assumed, it follows that the added monomer is distributed in the water and in the particle phase as

$$\dot{n}_i^P = \frac{\dot{n}_i K_i^P}{K_i^P + 1}. \quad (14)$$

The volume of the particle phase is additionally effected by contraction due to chemical reaction:

$$\frac{dV^P}{dt} = \sum_{j=1}^{k} \frac{\dot{n}_j \bar{V}_j K_j^P}{1 + K_j^P} + \sum_{j=1}^{k} R_j M_j \left(\frac{1}{\rho_{Pol}} - \frac{1}{\rho_j} \right). \quad (15)$$

In equation (13) the time derivative of V^P can be replaced by this expression.

For the observer design the model has to be reduced as the observability is bad if the derived equations for T_R, T_J, $[A]^P$, $[B]^P$, V^P, V^R and $[I]^R$ are considered. The distance to unobservability (DUO) (Eising, 1984; Rajamani and Cho, 1998) is used as a quantitative description of the observability of the system. It has to be noted, however, that the absolute values of this measure have to be compared to a reference point, e. g. a complex model. If the DUO for a reduced model derived from the complex one is larger, an observer based on the reduced model will perform better apart from the model mismatch of course.

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Definition 1. The distance to unobservability (DUO) of $(\mathbf{A}, \mathbf{C})$ is the magnitude of the smallest pertubation $(\mathbf{S}, \mathbf{T}) \in \mathbb{C}^{n \times n} \times \mathbb{C}^{n \times m}$, that makes the pair $(\mathbf{A} + \mathbf{S}, \mathbf{C} + \mathbf{T})$ unobservable:

$$\delta(\mathbf{A}, \mathbf{C}) = \inf_{(\mathbf{A}+\mathbf{S},\mathbf{C}+\mathbf{T}) \text{not observable}} \|[\mathbf{S}, \mathbf{T}]\|_2 . \quad (16)$$

Using Eising's relationship (Eising, 1984)

$$\delta(\mathbf{A}, \mathbf{C}) = \min_{\omega} \sigma_{\min} \begin{bmatrix} j\omega\mathbf{I} - \mathbf{A} \\ \mathbf{C} \end{bmatrix}, \quad (17)$$

the DUO can be calculated easily. As the process dynamics and the absolute values of the states change strongly with time, it is sensible to investigate the DUO dependent on the state variables.

If the differential equations of all states are considered, the distance to unobservability is always smaller than 10^{-4}.

For small sampling intervals of the measurements the jacket temperature can be assumed to be constant over the sampling period. Furthermore it is obvious that the differential equation for the initiator is stable and the differential equation for the reactor and polymer volume are unstable but controlled only by $\dot{n}$ and can thus be simulated with sufficient accuracy. They can be regarded as a non observable subsystem (Lopez-Arenas *et al.*, 1997). Hence the observer is based on the following reduced model:

$$\frac{dT_R}{dt} = \frac{1}{C_R} \left(\sum_i R_i(-\Delta H_i) + \sum_i \dot{n}_i M_i c_{p_i} \right.$$
$$\left. \times (T_{Rin} - T_R) + kA(T_J - T_R) \right) \quad (18)$$

$$\frac{d[i]^P}{dt} = \frac{1}{V^P + \frac{V^W}{K_i^P}} \left(\dot{n}_i - R_i - \frac{[i]^P}{K_i^P} \right.$$
$$\left((K_i^P - 1) \sum_{j=1}^k \frac{\dot{n}_j \bar{V}_j K_j^P}{1 + K_j^P} + \sum_{j=1}^k \dot{n}_j \bar{V}_j \right)$$
$$\left. - [i]^P \sum_{j=1}^k R_j M_j \left(\frac{1}{\rho_{Pol}} - \frac{1}{\rho_j} \right) \right). \quad (19)$$

For the same process conditions the distance to unobservability is improved, it is one order of magnitude larger than before. Figure 2 shows the dependency of the distance to unobservability (DUO) on the concentrations of monomer A and B in the particle phase.

From this figure it follows that it is not possible to observe every copolymerization process. There is a region where the total gross heat of reaction of both monomer reactions are similar. The lines h and k mark the edges of that region. The application of estimation techniques based on calorimetric data in this region is impossible, as the DUO decreases strongly and becomes zero when the relation (21) holds exactly, which means the process is unobservable. Hence state estimation cannot be used if
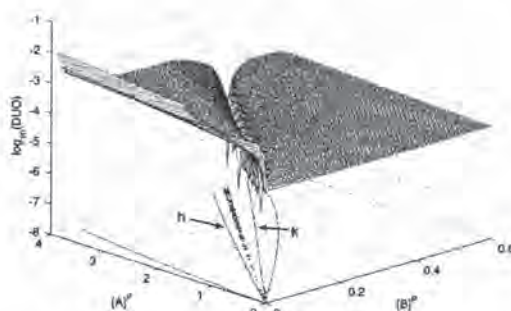

Fig. 2. Dependency of the distance to unobservability on the concentrations of the monomers in the particle phase

$$r_A(-\Delta H_A) \approx r_B(-\Delta H_B) \quad (20)$$
$$\Leftrightarrow \frac{r_A}{r_B} \approx \frac{(-\Delta H_B)}{(-\Delta H_A)}. \quad (21)$$

Equations (18) and (19) and the measurement equation are summarized as

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}) \quad (22)$$
$$\mathbf{y} = \mathbf{C}\mathbf{x}. \quad (23)$$

Here $\mathbf{x} = [T_R, [A]^P, [B]^P]^T$ is the state vector and $\mathbf{u} = [\dot{n}_A, \dot{n}_B, T_J]^T$ the vector of control inputs. The only available measurement is the reactor temperature, thus $\mathbf{C} = [1, 0, 0]$. The above description shows that when certain restriction are considered the process is observable from temperature measurements only. A state estimation technique can be applied for estimating the concentrations on the particle phase phase from temperature measurements.

5. ESTIMATOR DESIGN

The EKF is one of the most widely applied state estimation techniques in chemical engineering. In this approach zero mean random processes ξ and φ are introduced to the system and measurement equations:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}) + \xi \quad (24)$$
$$\mathbf{y} = \mathbf{C}\mathbf{x} + \varphi. \quad (25)$$

In our work we consider sampled data systems. Hence the ordinary differential equations have to be transformed to difference equations by integration over one sampling interval (Robertson *et al.*, 1996):

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \int_{t_k}^{t_{k+1}} \mathbf{f}(\mathbf{x}, \mathbf{u}) + \xi dt$$
$$\Longleftrightarrow \quad \mathbf{x}_{k+1} = \mathbf{F}(\mathbf{x}_k, \mathbf{u}_k) + \xi_k. \quad (26)$$

Due to the increase in computational speed and software improvements for solving optimization problems in the last decades, optimization based approaches have been developed (Jang *et al.*, 1986; Robertson *et*

al., 1996; Rao, 2000). If the sampling time is small it is difficult to apply optimization based state estimators which require the solution of a nonlinear dynamic program as computation time is limited. The Constrained Extended Kalman Filter (CEKF) is a special case of the Moving Horizon Estimator formulated by (Muske and Rawlings, 1994). If the measurement equation is linear, the following quadratic program has to be solved

$$\min_{\xi_{k-1,k},\varphi_{k,k}} \Psi_k = \hat{\xi}_{k-1,k}^T \mathbf{P}_{k,k-1}^{-1} \hat{\xi}_{k-1,k} + \hat{\varphi}_{k,k}^T \mathbf{R}^{-1} \hat{\varphi}_{k,k} \tag{27}$$

s.t.:
$$\hat{\mathbf{x}}_{k,k} = \hat{\mathbf{x}}_{k,k-1} + \hat{\xi}_{k-1,k}$$
$$\hat{\varphi}_{k,k} = y_k - \hat{\mathbf{x}}_{k,k}$$
$$\xi_{min} \le \hat{\xi}_{k-1,k} \le \xi_{max}$$
$$\varphi_{min} \le \hat{\varphi}_{k-1,k} \le \varphi_{max}$$
$$\mathbf{x}_{min} \le \hat{\mathbf{x}}_{k,k} \le \mathbf{x}_{max}.$$

$\hat{\mathbf{x}}_{i,j}$ describes the estimated state at time $t = t_i$ based on the measurements up to time $t = t_j$. The weighting matrices $\mathbf{P}_{k,k-1}$, $\mathbf{Q}$ and $\mathbf{R}$ are chosen similar to the weighting matrices of the EKF. $\mathbf{P}_k$ is thus calculated by the algebraic matrix Riccati equation.

$$\mathbf{P}_{k+1,k} = \mathbf{A}_{k,k} \left(\mathbf{P}_{k,k-1} - \mathbf{P}_{k,k-1} \mathbf{C}^T \right. \tag{28}$$
$$\left(\mathbf{CP}_{k,k-1} \mathbf{C}^T + \mathbf{R} \right)^{-1} \mathbf{CP}_{k,k-1} \right) \mathbf{A}_{k,k}^T + \mathbf{Q}.$$

with
$$\mathbf{A}_{k,k} = \left. \frac{\partial \mathbf{f}}{\partial \mathbf{x}} \right|_{\hat{\mathbf{x}}_{k,k}} \tag{29}$$

The prediction of the states is calculated by $\mathbf{x}_{k+1,k} = \mathbf{F}(\mathbf{x}_{k,k}, \mathbf{u}_k)$. The following constraints are taken into account:

- the concentrations of monomer A and B in the particle phase and the reactor temperature are larger than or equal to zero,
- the maximum reactor temperature is 100°C,
- the maximum concentrations of the monomers are calculated from the feed time, the feed rate and the initial volume of the particle phase:

$$[i]_{max}^P = \frac{\int_0^t \dot{n}_i dt}{V_{Pol,0} + \sum_{j=1}^n \int_0^t \dot{n}_j dt} \tag{30}$$

with $i,j = A,B$.

6. RESULTS

In the following we discuss the estimation results for Calorimetry and for the CEKF. The simulated data were computed with the complete model while the estimator and calorimetry are based on the simplified model. The filter parameters $\mathbf{P}_0$, $\mathbf{Q}$ and $\mathbf{R}$ were chosen by simulations. The initial states of the simulation and of the estimator are given in the figure captions.
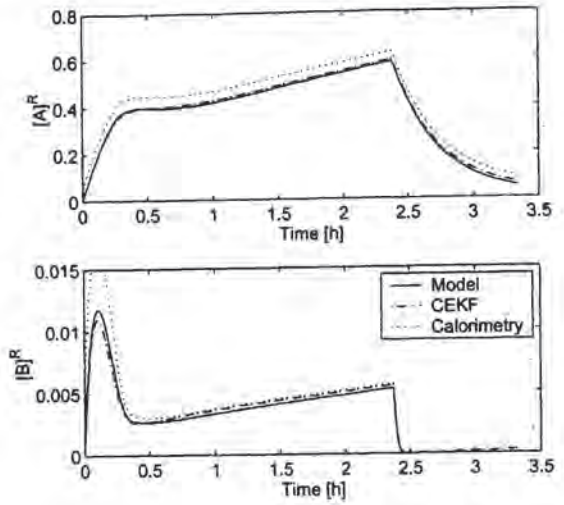

Fig. 3. Calorimetry and CEKF-estimation for given initial errors ($[A]_0^P = 0.05$, $[B]_0^P = 0.005$)

Figure 3 shows the difference between the calorimetry and the CEKF for wrong initial conditions.
It is clearly shown, that the CEKF can correct the error and reproduces the simulation data closely. Calorimetry, in contrast, diverges considerably. However, the initial values in seeded emulsion polymerization are normally well known, and mismatch between model and real parameters poses more serious problems.
Figures 4 and 5 show that the CEKF can cope well with deviations in ΔH_i and $\bar{n}$, while the calorimetry shows a serious deviation, which would prohibite its use in on-line control.
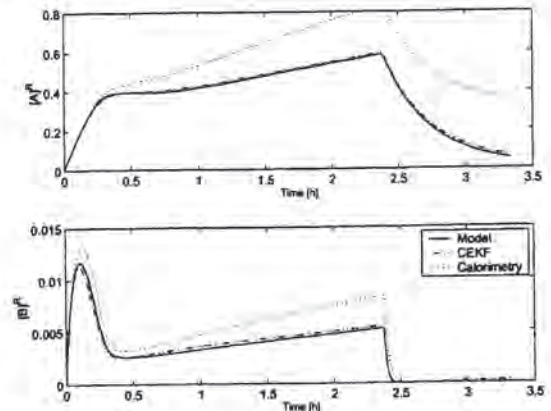

Fig. 4. Calorimetry and CEKF-estimation for plant model mismatch, 10% deviation in ΔH_i

The CEKF is generally robust due to the considered constraints. In figure 6, the estimation results of the CEKF for a combined parameter uncertainty are given. It is assumed that the reaction heat of each monomer and the efficiency factor for the decomposition of the initiator are not known exactly (a deviation of 10% is assumed). From figure 6 it can be seen that the estimation results are are still satisfactory and that the CEKF can thus be used to estimate the states of this
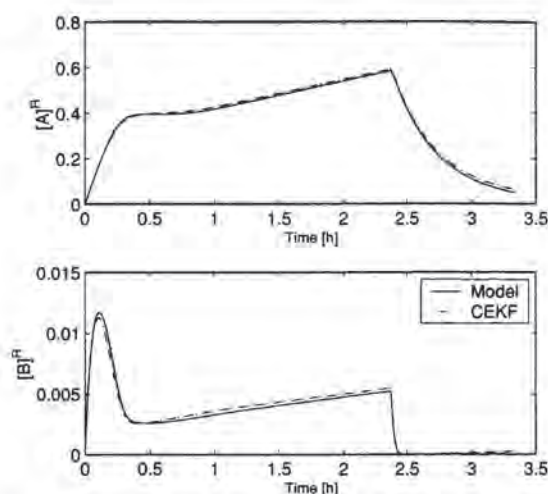
Fig. 5. Calorimetry and CEKF-estimation for plant model mismatch, 10% deviation in $\bar{n}$, realized through a change in $\bar{k}_t$
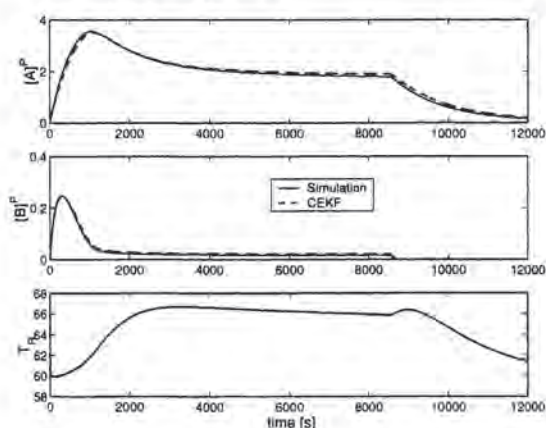

Fig. 6. CEKF-estimation, initial values $[A]_0^p = 0.05$, $[B]_0^p = 0.005$, $T_{R_0} = 63°$, deviations in the parameters ΔH_i and in the efficiency factor f process.

7. SUMMARY

We have shown that the CEKF approach is a suitable tool for the robust state estimation in an SCEP process using temperature data only. This is in contrast to feed-forward calorimetry, which only works well for precisely known initial conditions and parameters. Experimental data was simulated using a monodisperse model which describes all phases of the three-phase SCEP-process.

A simplified model was employed in the estimation. Due to to the use of feedback this simplified model serves well for state estimation and corrects initial condition errors as well as plant-model mismatch.

Despite its robustness, however, it was shown that the CEKF cannot be applied for all possible copolymerizations. The process is not observable when the product of polymerization rate and heat of reaction of the two monomers approaches equality.

We believe the described CEKF can be applied for real SCEP-processes and is a major step on the path to optimization and feedback control of SCEP, solely based on calorimetric data.

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