ELSEVIER

Chemical Engineering Science 60 (2005) 4233–4248

Chemical Engineering Science

www.elsevier.com/locate/ces

Simultaneous estimation of the heat of reaction and the heat transfer coefficient by calorimetry: estimation problems due to model simplification and high jacket flow rates—theoretical development

Stefan Krämer*, Ralf Gesthuisen

Innovene (BP Köln GmbH), Chemicals Production Köln, Postfach 750212, 50754 Köln, Germany

Received 11 December 2003; received in revised form 14 September 2004; accepted 4 February 2005
Available online 26 April 2005

Abstract

In batch and semi-batch reactors, the heat of reaction $\dot{Q}_R$ is normally estimated using calorimetry. If all temperatures and volumes are measured correctly and the measurements are filtered sensibly, the results are usually very good. For many applications, the overall heat transfer coefficient k also needs to be known. In heat balance calorimetry k and $\dot{Q}_R$ can be calculated simultaneously, if the correct model is used. It is shown that the commonly used model simplifications pose serious problems for large reactors. Subsequently a sensible model extension is discussed. For this extension we propose the application of an Extended Kalman Filter (EKF) to estimate the heat of reaction ($\dot{Q}_R$) and the heat transfer coefficient (k) simultaneously, as the EKF can handle the model extension well. Our emphasis lies on three important factors.

Firstly and mainly, the jacket of a jacketed reactor is generally modelled as a stirred tank. When looking at real jacketed reactors, the jacket behaves more like a plug-flow reactor. We propose a model extension to overcome this problem. Secondly, the heat transfer coefficient (k) is for many reactions strongly dependent on the batch time and should therefore also be estimated. With the usual models, errors may result which can be corrected by the model extension. Thirdly, the flow rate through the jacket and the hold-up in the reactor strongly influence the estimation quality. With a lower jacket flow rate estimation quality increases but cooling decreases, a trade-off has to be made. Using an EKF, good estimation quality can still be achieved for high flow rates. However, the trade-off is considered and the tuning is adjusted to the flow rate. An optimal flow rate calculation is suggested. Finally, it will be shown that adding measurements in the jacket rather than in the reactor will improve calorimetric estimation for the proposed model extension.

Keywords: Chemical reactors; Control; Extended Kalman filter; State estimation; Heat transfer; Calorimetry

1. Introduction

In batch and semi-batch stirred tank reactors, the heat of reaction is normally estimated using calorimetry. Calorimetric measurements offer a cheap and reliable way of identifying the heat of reaction, because the temperatures of the reaction medium and the cooling fluid are usually measured frequently. An extensive overview of the subject of calorimetry can be found in Weber (1974). Furthermore, heat balance calorimetry is used frequently for exothermic reactors and their control (Gugliotta et al., 1995; deBuruaga et al., 1997; Bartanek et al., 1999; Tauer et al., 1999; McKenna et al., 2000; Vicente et al., 2001).

A classical and widely applied method is reaction calorimetry, which employs the energy balances around a process to identify the heat of reaction. For most processes the determination of the heat of reaction is sufficient, but for the safe operation of exothermic reactions, knowledge of the heat transfer coefficient, which governs the rate of energy transferred between reactor and jacket, is also required. Often this value is needed for optimisation or control.

* Corresponding author. Tel.: +49 2133 556578; fax: +49 2133 557 133.
E-mail addresses: kraemer.stefan@gmx.de, stefan.kraemer@de.bp.com (S. Krämer).

0009-2509/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2005.02.060

When semi-batch polymerisation processes are considered as an example, strong variation in the overall heat transfer coefficient between reactor and jacket as well as the increase in heat transfer area have to be considered.

There are a few approaches to overcome this problem. Schmidt and Reichert (1988) simply estimate the derivatives of the temperatures and use a model to identify *kA*. *Oscillation calorimetry* can be used on laboratory scale reactors (Tietze et al., 1995, 1996a,b; Carloff et al., 1994; Luca and Scali, 2002). It separates the process dynamics influenced by the change of *kA* (fast dynamics) from the process dynamics influenced by the reaction rate (slow dynamics) and thus allows for their separate estimation. A more advanced heat balance calorimetric method was used by many authors (Guo et al., 2001; McKenna et al., 1996; Fevotte et al., 1998; McKenna et al., 2000; Othman et al., 2002; Krämer et al., 2003a,b), who use nonlinear observers to estimate $\dot{Q}_R$ and *kA* successfully. Santos et al. (2001), BenAmor et al. (2002) as well as Freire et al. (2004) use a so called "cascaded" observer to estimate both parameters. In this approach only an energy balance for the reactor and dummy derivatives for the heat of reaction and the heat transfer coefficient are used. Santos et al. (2001) state that this system of differential equations is unobservable from the reactor temperature measurement and therefore the authors have to assume that neither the heat of reaction nor the heat transfer coefficient vary quickly in the process to allow the cascaded observer to function at all. On the one hand, this assumption does not change the observability condition. On the other hand, it has to be noted that the stated system of differential equations used in Santos et al. (2001), BenAmor et al. (2002) and Freire et al. (2004) is globally observable as can be shown by a nonlinear analysis of the system. If the second derivative of the reactor temperature was used by the observer, both parameters could be observed in theory. Santos et al. (2001), BenAmor et al. (2002) and Freire et al. (2004) propose a different strategy to overcome this problem: They use a "cascaded" observer, which assumes one parameter (e.g., the heat of reaction) to be constant at one sampling point to estimate the other parameter (e.g., the heat transfer coefficient) and vice versa for the following sampling point. From a theoretic point of view in none of the mentioned papers the observability or the stability of the cascaded approach is investigated. Nonetheless, for the stated examples, they estimate both *k* and $\dot{Q}_R$ well.

The advantage of this approach is, of course, similar to oscillation calorimetry, i.e., no jacket balance is required. If a jacket balance is used, the jacket is assumed to behave like a CSTR.

In this paper, we use the proposed approach by Krämer et al. (2003b) to employ an Extended Kalman Filter (EKF) (Jazwinski, 1970; Gelb, 1974) to estimate the heat of reaction and the heat transfer coefficient. The basis of the analysis is formed by the classic equations of heat balance calorimetry, where a dynamic jacket heat balance is a requirement. In contrast to the cascaded observer we propose a simultaneous strategy to estimate the unknown parameters. This way, the global observability can be utilised and the local stability of the EKF is ensured. The EKF is known to give good and robust estimates and can be easily extended by the proposed model extension. However, it has to be noted that the proposed approach can be realised also with any other nonlinear state observers (e.g., Nonlinear Luenberger Observer, High Gain Observer, Nonlinear reduced observer).

As the EKF and calorimetry themselves are well known, the aims of this paper do not lie in explaining these concepts. We concentrate on the following points instead:

1. The jacket of a jacketed reactor is generally modelled as a stirred tank. When looking at pilot or industrial scale jacketed reactors, the jacket behaves more like a plug-flow reactor. Does this pose a problem and how is it overcome?
   As we focus on the problem of different jacked geometries and dynamics, other effects such as nonideal mixing in the reactor and additional equipment (e.g. condenser) are not considered.
2. The heat transfer coefficient (*k*) depends for many reactions strongly on the batch time. Can it be estimated well for different jacket geometries?
3. The flow rate through the jacket and the hold-up in the reactor strongly influence the eigenvalues of the linearised system matrices. Does this pose a problem for the EKF and how can we deal with it?

The main focus of this paper is point 1, the extension of the typically employed heat balance model to a model, in which non-ideal coolant flow regimes in the jacket are considered.

Point 3 is also very important. Maximum cooling depends on the jacket flow rate, as long as the heat transfer coefficient is high. If isothermal conditions are required in the reactor, a controller has to be used for the reactor temperature, the performance of which requires a large flow rate, as it uses the jacket inlet temperature as the manipulated variable.

As we will show, the estimation, but also the plant model mismatch depends on the flow rate, which has to be low for good estimation quality, and trade-offs have to be made.

The aims of this work are threefold:

Firstly, we will describe the typical heat balance model used around a stirred tank reactor, which considers the jacket behaving like a continuously stirred tank reactor (*from now on*: *CSTR*). This implies that there is no spatial distribution of temperature within the jacket. We will then extend this model by modelling the jacket as a plug flow reactor (*from now on*: *PFR*), which implies that there is a spatial temperature variation within the jacket from the inlet to the outlet. We consider this the realistic case for industrial scale reactors, as jackets of large reactors often have flow channels (as shown in Fig. 1 on p. 35 in the magnified section) or are realised as welded on half pipes.

Secondly, a state estimator is set up to estimate the heat of reaction and the heat transfer parameters. The state

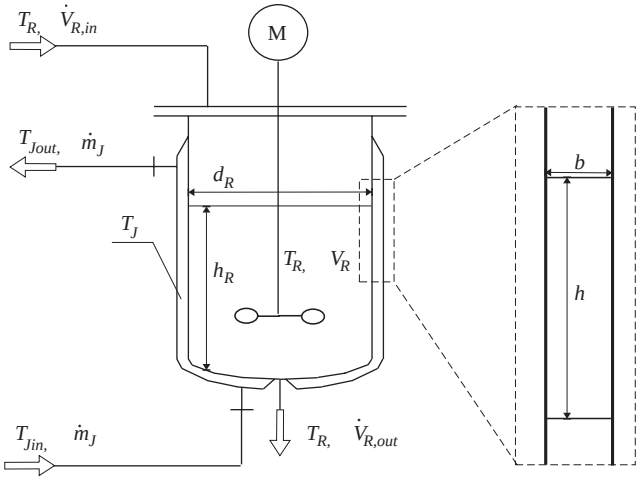

Fig. 1. Typical stirred tank diagram with labels. The magnified section explains the flow channels inside the jacket, from which PFR behaviour results in large tanks.

estimator will use a model assuming the jacket is a CSTR, whereas simulation will assume a PFR jacket. By looking at the linearisation and the estimation quality, important observations concerning the tuning will be reported. Additionally, the authors are unaware of any formal check of the observability conditions for a calorimetric estimator in the open literature. Therefore, global observability conditions will be checked.

Thirdly, the EKF model will be extended by the model for plug flow conditions in the jacket in order to improve the estimation quality resulting from plant model mismatch. The improved estimation will be shown in simulation studies.

Finally, considerations and calculations will be presented considering how the estimation quality can be further improved, both by adding additional temperature measurements, by sensor placement and by calculating an optimal flow rate.

2. Models

Consider a typical stirred tank reactor as shown in Fig. 1 on p. 35, symbols are explained in the list of symbols.

In all cases the reactor is assumed to be perfectly mixed and is therefore modelled as a CSTR. Differences in modelling occur for the jacket part. Firstly, the jacket is assumed to be perfectly mixed and is also balanced as a CSTR. Secondly, the jacket is not assumed to be perfectly mixed. Some general assumptions are made:

- It is assumed that the jacket is completely filled,
- the fluid is incompressible,
- the reactor is a cylinder, and
- to model a semi-batch reactor, the outflows of the reactor are simply set to zero.

2.1. The jacket behaviour is modelled as a CSTR

The mass and energy balances for a CSTR are set up as follows:

$$\text{Vessel:} \quad A_B \frac{\mathrm{d}h_R}{\mathrm{d}t} = \dot{V}_{R,\mathrm{in}} - \dot{V}_{R,\mathrm{out}}, \tag{1}$$

$$\begin{aligned}\frac{\mathrm{d}(C_R T_R)}{\mathrm{d}t} &= \dot{Q}_{R,\mathrm{in}} - \dot{Q}_{R,\mathrm{out}} + \dot{Q}_R - \dot{Q}_{R,\mathrm{loss}} - \dot{Q}_J,\\ &= \rho_{\mathrm{in}} c_{p,\mathrm{in}} \dot{V}_{R,\mathrm{in}} T_{R,\mathrm{in}} - \rho_R c_{p,R} \dot{V}_{R,\mathrm{out}} T_R\\ &\quad + \dot{Q}_R - \dot{Q}_{R,\mathrm{loss}} - kA(T_R - T_J).\end{aligned} \tag{2}$$

$$\begin{aligned}\text{Jacket} \quad \frac{\mathrm{d}T_J}{\mathrm{d}t} &= \frac{1}{m_J c_p} (\dot{Q}_{\mathrm{in}} - \dot{Q}_{\mathrm{out}} + \dot{Q}_J - \dot{Q}_{J,\mathrm{loss}})\\ &= \frac{1}{m_J c_{p,J}} (\dot{m}_J c_{p,J} (T_{J,\mathrm{in}} - T_J)\\ &\quad + kA(T_R - T_J) - \dot{Q}_{J,\mathrm{loss}}).\end{aligned} \tag{3}$$

$$\begin{aligned}\text{with :} \quad A &= A_B + \pi d_R h_R\\ &= \frac{\pi}{4} d_R^2 + \pi d_R h_R.\end{aligned} \tag{4}$$

The term C_R describes the absolute heat capacity of the reactor, its contents and inserts and has to be identified for each system separately. If the densities and heat capacities can be considered the same, the balances can be significantly simplified.

2.2. The jacket behaviour is modelled as a PFR

The problem is modelled by assuming that the jacket behaves like a PFR. If the reactor is not completely filled, no heat is exchanged between reactor and jacket in the upper part of the vessel, as the heat transfer from the gaseous phase to the jacket is negligible compared to the heat transfer from the liquid phase to the jacket. Therefore, this upper part is modelled separately just considering the convective term, which means it is simply a time delay (modelling this time delay is important for good estimation). Balancing a finite volume of the PFR yields the following equations (development details are given in the Appendix):

$$\begin{aligned}\text{Vessel :} \quad &\frac{\mathrm{d}(C_R T_R)}{\mathrm{d}t}\\ &= \dot{Q}_{R,\mathrm{in}} - \dot{Q}_{R,\mathrm{out}} + \dot{Q}_R - \dot{Q}_{R,\mathrm{loss}} - \dot{Q}_J\\ &= \rho_{\mathrm{in}} c_{p,\mathrm{in}} \dot{V}_{R,\mathrm{in}} T_{R,\mathrm{in}} - \rho_R c_{p,R} \dot{V}_{R,\mathrm{out}} T_R\\ &\quad + \dot{Q}_R - \dot{Q}_{R,\mathrm{loss}} - \dot{Q}_J,\end{aligned} \tag{5}$$

$$\begin{aligned}\text{Lower jacket :} \quad &\frac{\partial T_{J,L}}{\partial t}\\ &= -v \frac{\partial T_{J,L}}{\partial z} + \frac{k}{b \rho_J c_{p,J}} (T_R - T_{J,L})\\ &\quad - \frac{\dot{q}_{J,\mathrm{loss}(z)}}{b \rho_J c_{p,J}},\end{aligned} \tag{6}$$

$$\text{Upper jacket}: \quad \frac{\partial T_{J,U}}{\partial t} = -v\,\frac{\partial T_{J,U}}{\partial z} - \frac{\dot{q}_{J,\text{loss}}(z)}{b\rho_J c_{p,J}}, \tag{7}$$

$$\text{Jacket loss}: \quad \dot{Q}_{J,\text{loss}} = \int_0^{L_{\max}} \dot{q}_{J,\text{loss}}(z)\mathrm{d}z.$$

The length of the upper part of the jacket is given by $L_{\max} - L$, whereas L corresponds to the length of the lower part and $L_{\max}$ is the total length of the jacket.

$$L = \frac{A}{h}, \tag{8}$$

$$L_{\max} = \frac{A_{\max}}{h}. \tag{9}$$

If this system is to be simulated, the manipulated variables for the jacket ($T_{J,\text{in}}$) as well as the heat flow are needed. *For the lower part of the jacket*, the manipulated variable is the boundary condition for Eq. (6) and $\dot{Q}_J$ is found by integrating the heat transfer of every balanced volume element $\mathrm{d}z$ up to length L.

$$\text{Boundary}: \quad T_{J,L}(0,t) = T_{J,\text{in}}(t), \tag{10}$$

$$\text{Heat flow}: \quad \dot{Q}_J = \int_0^L kh(T_R - T_{J,L}(z))\,\mathrm{d}z. \tag{11}$$

The upper part of the jacket is also modelled as a PFR. The boundary condition for Eq. (7) is given by:

$$\text{Boundary}: \quad T_{J,L}(L,t) = T_{J,U}(0,t). \tag{12}$$

As back mixing in the jacket can be neglected in most cases, Eqs. (6) and (7) describe the 'true' behavior of the jacket especially if the cooling device is realised as a half pipe welded to the wall of the reactor.

2.3. Estimation model

Generally, models where the jacket is assumed to be perfectly mixed, i.e., behave like a CSTR, are used for calorimetry. If calorimetry is performed by a state estimator, the estimated heat of reaction $\dot{Q}_R$ and heat transfer coefficient k have to be treated as parameters. The model has to be separated into an observed and unobserved submodel. The unobserved submodel consists of the differential equation for the liquid level in the tank, which is only simulated (or measured). If the liquid level is simulated or measured, it can be considered an input to the state estimator model. For an EKF, sampled measurement systems are considered. The heat capacity (C_R) is then only changed by the volume increase, not by the reactor content composition. An average $c_{p,R}$ and ρ_R are calculated and considered constant for one time step. If the sampling time is chosen accordingly such that the composition in the tank will not change as rapidly as the temperatures, this is a plausible assumption. Eq. (2) can then be simplified using Eq. (1) and

$$C_R = m_S c_{p,S} + A_B h_R \rho_R c_{p,R} \tag{13}$$

to yield

$$\begin{aligned}\frac{\mathrm{d}T_R}{\mathrm{d}t} = {} & \frac{\dot{V}_{R,\text{in}}}{m_S c_{p,S} + A_B h_R \rho_R c_{p,R}} \\ & \times (\rho_{\text{in}} c_{p,\text{in}} T_{R,\text{in}} - \rho_R c_{p,R} T_R) \\ & + \frac{1}{m_S c_{p,S} + A_B h_R \rho_R c_{p,R}} (\dot{Q}_R - \dot{Q}_{R,\text{loss}}) \\ & - \frac{kA}{m_S c_{p,S} + A_B h_R \rho_R c_{p,R}} (T_R - T_J).\end{aligned} \tag{14}$$

For the sake of clarity, we have assumed that $m_S c_{p,S}$ (heat capacity of the reactor wall and possible inserts) is negligible and $\rho_R c_{p,R} = \rho_{\text{in}} c_{p,\text{in}}$, an assumption which generally should not be made in practice. If the heat capacities of the different components in the reactor and the feed are very different, this simplification cannot be made.

The above stated simplifications yield the model

$$\begin{aligned}\frac{\mathrm{d}T_R}{\mathrm{d}t} = {} & \frac{\dot{V}_{R,\text{in}}}{V_R}(T_{R,\text{in}} - T_R) + \frac{\dot{Q}_R - \dot{Q}_{R,\text{loss}}}{V_R \rho_R c_{p,R}} \\ & - \frac{kA}{V_R \rho_R c_{p,R}} (T_R - T_J)\end{aligned} \tag{15}$$

and the unaltered Eqs. (3) and (4) for the jacket and heat transfer area.

The aim of calorimetry is to find $\dot{Q}_R$. However, k is generally also unknown. Therefore, k is also observed. The model used in the observer is therefore extended by the following two equations, which allow for the estimation of $\dot{Q}_R$ and k, which are considered parameters in the estimation problem.

$$\frac{\mathrm{d}\dot{Q}_R}{\mathrm{d}t} = 0, \tag{16}$$

$$\frac{\mathrm{d}k}{\mathrm{d}t} = 0. \tag{17}$$

All models have been extended by a geometry factor to allow for scale-up, $f_G = 1$ means a 10 l-reactor is used. The model including f_G can be found in Appendix B.

2.4. Model analysis

2.4.1. Observability

The first step in the observer design is to check the observability of the considered dynamic system. A system is said to be observable if an initial state $\mathbf{x}(t=0) = \mathbf{x}_0 \in \mathbf{X}_0$ can be determined by the knowledge of the inputs $\mathbf{u}(t)$ and the measurements $\mathbf{y}(t)$ in the interval $0 < t < t_1$. This means that the complete state vector (here: $\mathbf{x} = (T_R, T_J, \dot{Q}_R, k)^{\mathrm{T}}$) could be re-constructed at a time t using the historic and current measurement $\mathbf{y}(t) = (T_R, T_J)^{\mathrm{T}}$ and the model by reconstructing first $\mathbf{x}_0$ and then simulating up to time t. In practice, these steps are inherent in the recursive structure of state estimators. For nonlinear dynamic systems, conditions to check this property can be found in Walcott et al. (1987) or Birk (1992).

For the above model (15)–(17) as well as (3) and (4), the global observability can be checked (A is replaced by $\pi r_R^2 + \frac{2V_R}{r_R}$). Using the method presented by e.g., Birk (1992), a nonlinear observability map can be identified:

$$y_1 = T_R, \tag{18}$$

$$y_2 = T_J, \tag{19}$$

$$\dot{y}_1 = \frac{\dot{V}_{R,\text{in}}}{V_R}(T_{R,\text{in}} - T_R) + \frac{\dot{Q}_R - \dot{Q}_{R,\text{loss}}}{V_R \rho_R c_{p,R}} - \frac{k(\pi r_R^3 + 2V_R)}{r_R V_R \rho_R c_{p,R}}(T_R - T_J), \tag{20}$$

$$\dot{y}_2 = \frac{\dot{m}}{m}(T_{J,\text{in}} - T_J) + \frac{k(\pi r_R^3 + 2V_R)}{r_R m c_p}(T_R - T_J) - \frac{\dot{Q}_{J,\text{loss}}}{m c_p}. \tag{21}$$

This leads to an equation system with six unknowns (T_R, T, $\dot{Q}_R$, $\dot{Q}_{R,\text{loss}}$, $\dot{Q}_{J,\text{loss}}$, k) and four equations. Assuming $\mathbf{y}$ and all its derivatives w.r.t. time are available from measurements an equation system results which is solvable for the desired values $\dot{Q}_R$ and k to yield:

$$k = \frac{\dot{m} c_p \dot{y}_2 - \dot{m} c_p (T_{J,\text{in}} - y_2) + \dot{Q}_{J,\text{loss}}}{\frac{\pi r_R^3 + 2V_R}{r_R}(y_1 - y_2)}, \tag{22}$$

$$\dot{Q}_R - \dot{Q}_{R,\text{loss}} = V_R \rho_R c_{p,R} \left(\dot{y}_1 + \frac{k(\pi r_R^3 + 2V_R)}{r_R V_R \rho_R c_{p,R}} \times (y_1 - y_2) - \frac{\dot{V}_{R,\text{in}}}{V_R}(T_{R,\text{in}} - y_1) \right). \tag{23}$$

This system is globally observable for every T_R and T_J except for $T_R = T_J$. If k is known, Eq. (22) becomes unnecessary and the system is globally observable. The result of the inverse observability map can be used to compare its results and the results of a well-tuned EKF (Franke, 2000; Krämer et al., 2001).

Additionally in order to receive sensible information, the bias terms $\dot{Q}_{R,\text{loss}}$ and $\dot{Q}_{J,\text{loss}}$ need to be known.

It is important to distinguish between the reactor and the jacket heat loss. Let us first consider the estimation of $\dot{Q}_R$. This heat of reaction cannot be estimated by itself in the above estimation scheme. However, if Eq. (22) is inserted in Eq. (23), the following results:

$$\dot{Q}_R - \dot{Q}_{R,\text{loss}} - \dot{Q}_{J,\text{loss}} = V_R \rho_R c_{p,R} \left(\dot{y}_1 + \frac{\dot{m} c_p \dot{y}_2 - \dot{m} c_p (T_{J,\text{in}} - y_2)}{V_R \rho_R c_{p,R}} - \frac{\dot{V}_{R,\text{in}}}{V_R}(T_{R,\text{in}} - y_1) \right). \tag{23a}$$

This means that only the sum of all the different heat generation terms can be estimated. This estimation is independent of the estimation of k. The loss terms can be identified during a period where no reaction takes place (for example while heating the tank) and then used as a bias term. For the estimation of $\dot{Q}_R$, the distinction between the different origins of the heat loss is irrelevant. For a more advanced technique to determine the heat losses, the interested reader is referred to Othman et al. (2002).

The situation is different for the estimation of k. Here, a heat loss from the tank has no influence, whereas a heat loss from the jacket influences its estimation. In order to receive good results, the considered tank has to be known well, a situation which might pose problems in practice. If one of the loss terms is negligible, the other can be estimated during a period with no heat of reaction and used as a bias or input term. If the terms both have a similar value which is not negligible, good estimation quality cannot be guaranteed. However, when the method is applied to a real reactor, these flaws can be identified before the method is applied. For an industrial jacketed tank, heat loss from the tank can probably be neglected or modelled if heat is lost through the lid or by evaporation. Then only $\dot{Q}_{J,\text{loss}}$ is estimated before the reaction starts. A well insulated jacketed tank probably has generally negligible heat loss.

We therefore develop our method with this problem in mind but using the simplification $\dot{Q}_{J,\text{loss}} = 0$ and $\dot{Q}_{R,\text{loss}} = 0$ without loss of generality for the proposed estimator and jacket model extension, as these terms are linear bias terms, which can be added after the estimation if required.

A further matter, which is of practical importance but does not affect the theoretical results, is the situation in small lab scale reactors. For very high flow rates in the jacket, the measurements of the jacket inlet and the jacket outlet stream appear identical, as their difference is beyond the measurement resolution. This does not change the global observability map and the observability of the system theoretically. From a practical view point, however, observation will not work at high flow rates due to measurement limitations, i.e., too large a system noise. Then, k cannot be estimated in practice.

The inverse observability map describes the solution an observer is converging to. Incidentally, the results of the global observability map are also the equations used in standard heat balance calorimetry. $\dot{Q}_R - \dot{Q}_{R,\text{loss}} - \dot{Q}_{J,\text{loss}}$ is observable by itself, even for $T_R = T_J$; $(T_R - T_J)$ should be eliminated by inserting k into Eq. (23). Therefore, for perfect signals, an observer would not be necessary if the inverse observability map can be identified, as the correct solution can always be inferred. However, even if this is the case, the definition space here has one exception ($T_R = T_J$). These equations are therefore not useful to estimate k if situations arise where $T_R \approx T_J$. An observer cannot estimate k in that region, either, but its smoothing and simulation capabilities avoid a division by zero.

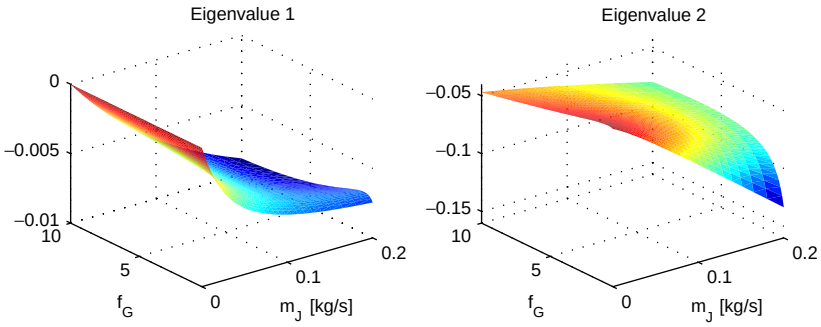

Fig. 2. Eigenvalues plotted vs. f_G and $\dot{m}_J$ for a small range of these values.

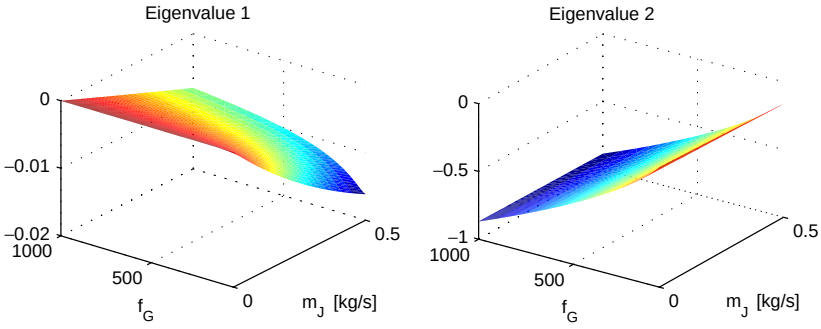

Fig. 3. Eigenvalues plotted vs. f_G and $\dot{m}$ for a large range of these values.

2.4.2. Eigenvalues of the linearised system

An EKF uses a linearised system for the estimation. It is therefore interesting for the tuning of the filter to consider the change in the eigenvalues of the linearised system with design parameters. The design parameters considered here are the jacket flow rate $\dot{m}_J$ and the geometry factor f_G.

Of these two factors, f_G is a design factor decided when building the plant. $\dot{m}_J$ is normally constant for jacketed reactors and $T_{J,\text{in}}$ is regulated. However, $\dot{m}_J$ is easily changed in an existing plant. Its possible change needs to be considered.

The eigenvalues of the linearised system matrix provide information about the system's dynamic behaviour in close proximity of a considered state and dependent on the system's parameters, design parameters and states. If they change strongly, it may be necessary to adjust the weighting matrixes (covariance matrices) of the EKF. For simplicity, the following analysis is performed for model (15) and the jacket balance (3).

If the eigenvalues of the linearisation matrix are checked, it becomes obvious that the design variable $\dot{m}_J$ has a large influence on the dynamics of the system. As it can be manipulated over a large range, this influence has to be considered. It should be noted that changes in $\dot{m}_J$ do not influence the global observability of the system but may influence estimation quality.

In the system described, 2 eigenvalues are below zero and two eigenvalues are zero. When talking about an increase in eigenvalues, it means that the eigenvalue in question moves closer towards zero, i.e., its absolute value decreases, the time constants of the system increase and it becomes slower!

As can be seen in Fig. 2, eigenvalue 1 decreases considerably with an increase of $\dot{m}_J$. This effect is not changed by a large geometry as can be seen in Fig. 3. This behaviour is expected as a small $\dot{m}_J$ increases the residence time of the jacket fluid. The reactor dynamics are only influenced by the jacket flow rate for small geometries due to the volume to area ratio. It can be deduced that the observer gain needs to be adjusted to the jacket flow rate. With this eigenvalue so close to zero it governs the system dynamics, i.e., the flow rate defines the slow and therefore governing dynamics of the system.

A similar effect can be seen when looking at the geometry factor. Its increase decreases eigenvalue 2. As the absolute value is significantly larger than eigenvalue 1, it does not govern the dynamics. The mass flow rate in the jacket has virtually no influence on this eigenvalue whereas the geometry increases the second time constant.

3. Simulation study I

3.1. Simulation

An EKF is used here to estimate the process parameters $\dot{Q}_R$ and k. $\dot{Q}_R$ and k are set as would be expected in a typical semi-batch polymerisation process. In such a process

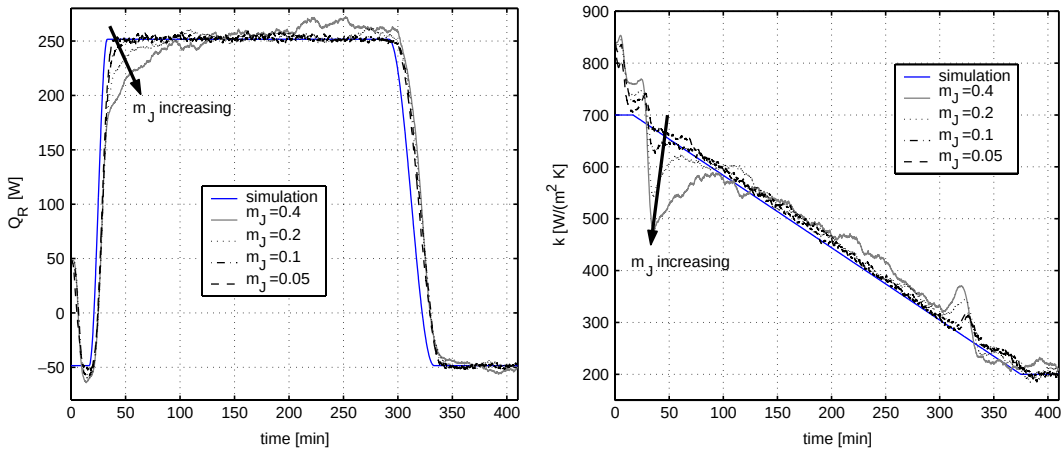

Fig. 4. Estimation for a 10 l reactor with constant covariance matrix **Q**. *Please note that m_J in the figure is indeed $\dot{m}_j$ in* kg/s.

the heat transfer coefficient depends on the viscosity and therefore on the conversion of the monomers. To show a more realistic estimation problem, the temperature in the reactor is controlled by a PI-controller, which can manipulate the jacket feed temperature. This manipulated variable itself is subject to a cascade controller within a heating and cooling apparatus. To model this behaviour, the real T_{in} follows its set point like a first order transfer function (PT1-behaviour) with a time constant of 690 s. While the different mass flow rates were scaled for larger reactors, these values were kept the same. The model with the PFR jacket has been used for simulation.

3.2. Extended Kalman Filter equations

Mathematical modelling of dynamic systems often yields nonlinear differential equations off the form:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}) + \xi(t),$$

$$\mathbf{x}(0) = \mathbf{x}_0 + \xi_0, \tag{24}$$

$$\mathbf{y}(t) = \mathbf{h}(x) + \varphi(t), \tag{25}$$

where $\mathbf{x}$, $\mathbf{u}$, $\mathbf{y}$, ξ and φ are the n-dimensional state vector, the r-dimensional vector of control variables, the m-dimensional measurement vector and n-dimensional vectors of the model and measurement errors, respectively. The EKF is one of the most frequently applied state estimation techniques in chemical engineering. In this approach ξ and φ are assumed to be zero mean random processes.

In our work we consider sampled systems. Hence the ordinary differential equations have to be transformed to difference equations by integration over one sampling interval:

$$\begin{aligned}\mathbf{x}_{k+1} &= \mathbf{x}_k + \int_{t_k}^{t_{k+1}} (\mathbf{f}(\mathbf{x}, \mathbf{u}) + \xi)\, \mathrm{d}t, \\ &= \mathbf{F}(\mathbf{x}_k, \mathbf{u}_k) + \xi_k, \end{aligned} \tag{26}$$

$$\mathbf{y}_k = \mathbf{h}(\mathbf{x}_k) + \varphi_k. \tag{27}$$

The discrete linear Kalman Filter is based on the solution of the minimization of the expected values of the estimation error and as such is optimal for the provided covariance matrices. As the Kalman Filter can also be formulated as an optimal state regulator problem, the covariance matrices **Q** and **R** can be generally considered as weighting matrices of the estimation errors. The solution to this optimisation problem can be found in the Matrix–Riccati-equation.

The EKF is similarly found. The linear model equations in the prediction are replaced by the nonlinear process model, the prediction of the weighting matrix $\mathbf{P}_{k+1|k}$ is performed by Taylor-linearizing the process model. Its equations are written as:

Correction terms:

$$\mathbf{K}_k = \mathbf{P}_{k|k-1}\mathbf{H}_{k|k-1}^{\mathrm{T}}(\mathbf{H}_{k|k-1}\mathbf{P}_{k|k-1}\mathbf{H}_{k|k-1}^{\mathrm{T}} + \mathbf{R})^{-1}, \tag{28}$$

$$\hat{\mathbf{x}}_{k|k} = \hat{\mathbf{x}}_{k|k-1} + \mathbf{K}_k(\mathbf{y}_k - \mathbf{h}(\hat{\mathbf{x}}_{k|k-1})), \tag{29}$$

$$\mathbf{P}_{k|k} = (\mathbf{I} - \mathbf{K}_k\mathbf{H}_{k|k-1})\mathbf{P}_{k|k-1}. \tag{30}$$

Prediction terms:

$$\hat{\mathbf{x}}_{k+1|k} = \mathbf{F}(\hat{\mathbf{x}}_{k|k}, \mathbf{u}_k), \tag{31}$$

$$\mathbf{P}_{k+1|k} = \mathbf{A}_{k|k}\mathbf{P}_{k|k}\mathbf{A}_{k|k}^{\mathrm{T}} + \mathbf{Q}, \tag{32}$$

with:

$$\mathbf{A}_{k|k} = \left.\frac{\partial \mathbf{F}}{\partial \mathbf{x}}\right|_{\hat{\mathbf{x}}_{k|k}}, \tag{33}$$

$$\mathbf{H}_{k|k-1} = \left.\frac{\partial \mathbf{h}}{\partial \mathbf{x}}\right|_{\hat{\mathbf{x}}_{k|k}}. \tag{34}$$

Here, the model equations are (15)–(17) as well as (3) and (4) with $\dot{Q}_{J,\text{loss}} = 0$ and $\dot{Q}_{R,\text{loss}} = 0$.

3.3. Tuning of the EKF

Figs. 4 and 5 present results of the estimation. Only the estimated of the unmeasured parameters $\dot{Q}_R$ and k are shown,

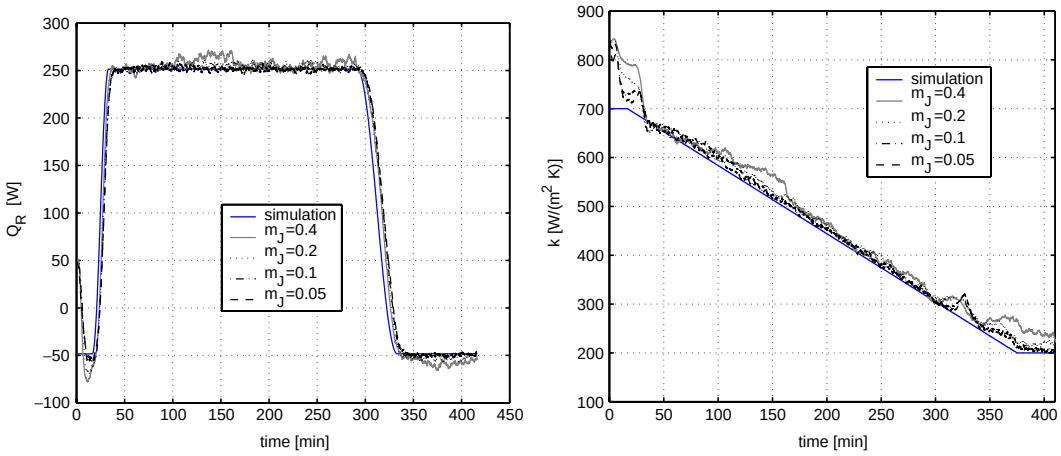

Fig. 5. Estimation for a 10 l reactor with adjusted covariance matrix **Q**. *Please note that m_J in the figure is indeed $\dot{m}_j$ in* kg/s.

as the temperatures are measured. Measured data are T_R and T_J which are disturbed by random measurement noise of ± 0.1 K. Initial conditions were offset by 100 W. The needed quantities V_R and h_R are considered measured.

The filter was tuned using the covariance of the measurement error for matrix **R** and adjusting matrix **Q** by hand, until good agreement between estimation and simulation was reached.

It can be clearly seen in Fig. 4 that the changing jacket flow rate results in a change in estimation quality if the elements of **Q** are fixed.

The observer dynamics should always be faster than the system dynamics as an asymptotic behaviour towards the real values is not possible otherwise. As the jacket flow rate decreases the governing time constant of the system, the weighting matrix **Q** for the EKF has to be adjusted accordingly.

q_{33} and q_{44} in this example show a direct influence on the two estimated parameters. As the estimation of $\dot{Q}_R$ is the more important parameter, emphasis was placed on q_{33}. The lines in Fig. 4 identify the problem of the estimator when flow rates are high. The estimation results for $\dot{Q}_R$ deviate too far from the real data and would pose problems if these $\dot{Q}_R$ data were used for estimating concentrations with an additional open loop model.

The estimation of $\dot{Q}_R$ is strongly influenced by the jacket flow rate. We have therefore adapted the element q_{33} of the tuning matrix Q of the EKF by a factor $\dot{m}/\dot{m}_{\min}$ which compensates the eigenvalue change by increasing the amplification. This way, $\dot{Q}_R$ is corrected more strongly. This adjustment also improved the estimation quality of k. This also leads to a larger or smaller amplification of measurement noise and may pose a problem with very large flow rates and a small $\Delta T_J = T_{J,\text{in}} - T_{J,\text{out}}$.

The physical interpretation of this change can be given as follows: An increase in jacket mass flow rate reduces the resulting ΔTs which is directly used in the state estimation scheme and directly reflects $\dot{Q}_R$. It can be clearly seen that this adaptation improves the estimation result. The EKF is now capable to produce good estimation results for different flow rates.

The analysis of the adjustment of **Q** have all been performed for a geometry factor of $f_G = 1$. As $\dot{m}_J$ is adjusted to the size scaling and only the equivalents to $\dot{m}_J = 0.05$ kg/s and $\dot{m}_J = 0.2$ kg/s are used, $\dot{m}_J$ is from now on labelled *high* and *low*.

3.4. Estimation quality for plant model mismatch

The simulations shown in this section are based on a jacket, which behaves like a PFR, the EKF, however, uses the much simpler model, in which the jacket behaves like a CSTR. The covariance matrix **Q** has been adjusted as described above.

For further analysis, simulation studies with different geometries as well as different jacket flow rates where conducted. Temperatures were simulated and random noise was added (± 0.1 K). Fig. 6 shows that a correct estimation of k depends strongly on the jacket flow rate. The estimation improves with higher flow rate as the plant model mismatch is decreased while the adjusted EKF copes with the problem of a higher flow rate.

It is now important to consider how the reactor size influences the estimation quality. The considered 10 l reactor was therefore scaled by the geometry factor f_G to volumes of 2 and 20 m^3. Fig. 7 shows the results for these cases and clearly demonstrates that a change in reactor size leads to an increasingly inaccurate estimation of the heat transfer coefficient k and the heat of reaction $\dot{Q}_R$.

3.5. Intermediate conclusions

Heat balance calorimetry is a means to estimate the heat of reaction and the heat transfer coefficient. Alternatively, the model can be used in a state estimation scheme to

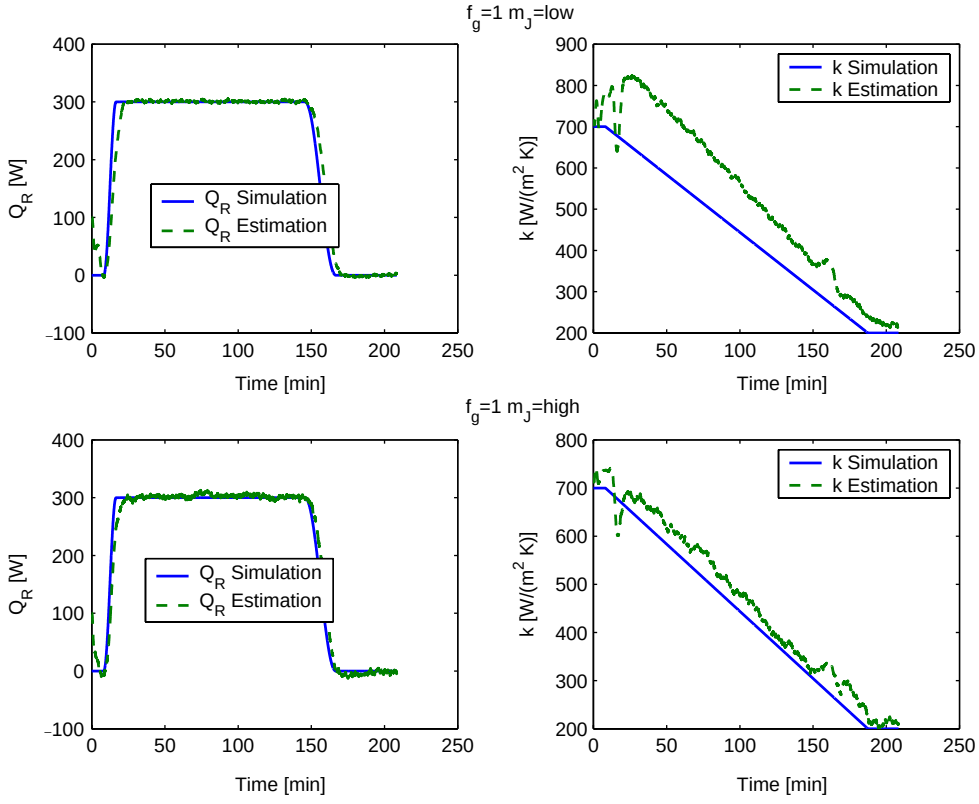

Fig. 6. Estimation using a 10 l reactor with low (top line) and high (bottom line) mass flow rates. *Please note that m_J in the figure is indeed $\dot{m}_j$ in* kg/s.

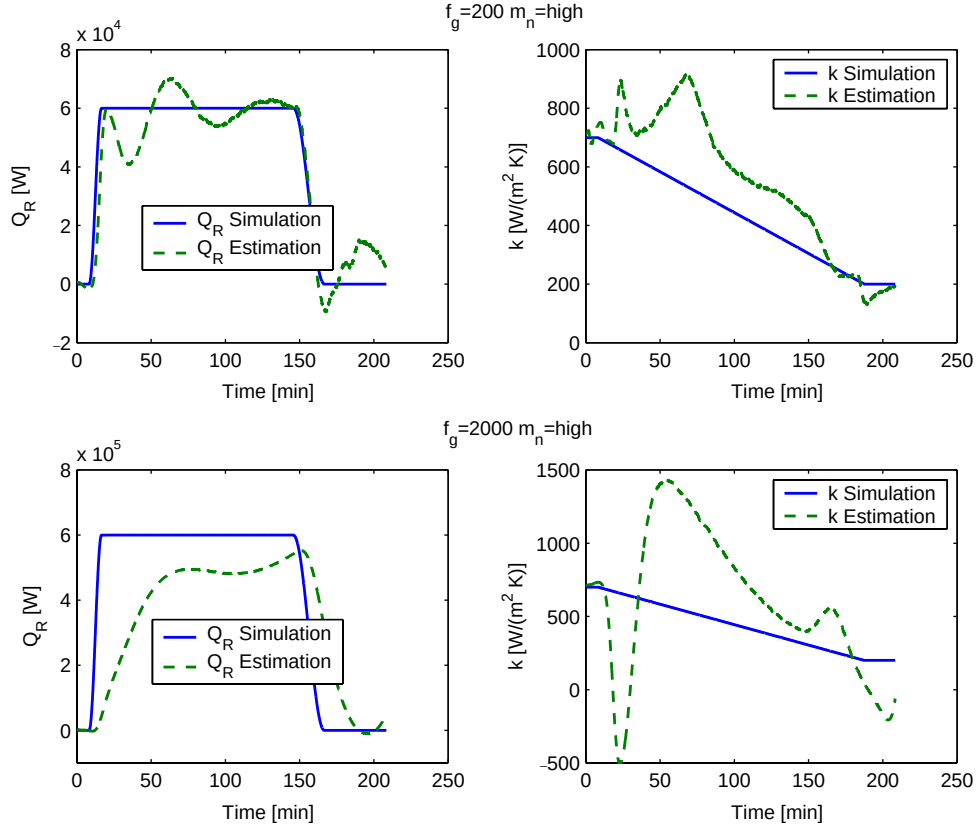

Fig. 7. Simulation and estimation of a $2\,m^3$ (top line) $20\,m^3$ (bottom line) reactor with high jacket mass flow rates.

estimate k and $\dot{Q}_R$ as parameters. The model used is globally observable if $T_R \neq T_J$. However, for large reactors the jacket of a jacketed reactors does not behave like a CSTR. If this model mismatch is not considered in the estimation and the reactor size is increased, the estimation quality is dramatically decreased. It is therefore necessary to develop a model which can be used in the EKF and takes the PFR behaviour of the jacket into account.

4. Model and estimation extension

The PFR behaviour in the jacket can be approximated well by discretisation using orthogonal collocation (Villadsen and Michelsen, 1978; Krämer et al., 2003a). In order to yield a simple and not too large model it is sufficient to use four internal collocation points resulting in five differential equations for the lower part of the jacket instead of one. Such a discretised model shows good accuracy (Georgakis et al., 1977). It has also been shown that orthogonal collocation preserves observability (Gesthuisen and Engell, 2000). Therefore, this method is a suitable approach for the problem at hand. The application of the orthogonal collocation yields:

$$\frac{\mathrm{d}}{\mathrm{d}t} X(t) = -\frac{\dot{m}}{bhL\rho}\mathbf{B}X(t) - \frac{\dot{m}}{bhL\rho}\mathbf{B}_{z=0}x(t, z=0) + \frac{k}{\rho c_p b} F(X(t)). \tag{35}$$

with

$$X(t) = \begin{pmatrix} T_J(z=z_1) \\ T_J(z=z_2) \\ \vdots \\ T_J(z=z_{p+1}) \end{pmatrix} \tag{36}$$

and

$$F(X(t)) = \begin{pmatrix} (T_R - T_J(z=z_1)) \\ (T_R - T_J(z=z_2)) \\ \vdots \\ (T_R - T_J(z=z_{p+1})) \end{pmatrix}, \tag{37}$$

p is the number of internal collocation points and z describes the space domain. $\mathbf{B}$ are the collocation matrices. Therefore, z_{p+1} corresponds to the effective length of the jacket pipe, up to where exchanging heat is possible. The expression for $\dot{Q}_J$, with

$$\dot{Q}_J = \int_0^L kh(T_R - T_J(z))\,\mathrm{d}z, \tag{38}$$

is left to be determined. There are two ways of calculating the integral: Integrating the resulting polynomial or approximating by trapezoid or Simpson's rule. Here the choice was trapezoid rule.

The model describing the upper part of the jacket is solved for one collocation point. Discretising the equation for the upper part of the jacket results in the subsequent expression:

$$\frac{\mathrm{d}T_J}{\mathrm{d}t} = -\frac{\dot{m}}{bh\rho(L_{\max} - L)}(T_J - T_J(z=z_{p+1})). \tag{39}$$

This model is subsequently used in the EKF.

5. Simulation study II

Using model (5)–(12) for simulation with the jacket equation discretisation shown in Eqs. (35)–(37) in the EKF, the estimation for the 2 m^3 reactor is repeated for two different jacket flow rates. Note the improvement over the results in Fig. 7.

As Fig. 8 clearly shows, the estimation of k and $\dot{Q}_R$ is dramatically improved. It should be noted that the simulation was also performed using orthogonal collocation, however, the EKF model uses fewer collocation points and these points do not coincide, which corresponds to a certain plant model mismatch.

6. Additional considerations

It has been shown above that the simultaneous estimation of the heat transfer coefficient and the heat of reaction depends on the reactor geometry and the jacket flow rate.

These considerations lead to the question if an optimal flow rate calculation might be necessary. Furthermore, additional sensor placement might be considered to improve the estimation quality. If additional sensors are used, this furthermore leads to the question where they should be placed. And finally, the considerations so far have been concerned with near ideal jacket configurations, either a CSTR behaviour (bath) or a PFR behaviour (welded half pipes). How can other geometries be accounted for?

6.1. Optimal flow rate calculation

We address the practical problem of the decreasing estimation quality with high jacket flow rates by calculating an "optimal" $\dot{m}_J$, which is highly relevant, as it poses a limit beyond which observation becomes practically impossible. Thus, if $\dot{m}_J$ is regulated, the optimal value provides an upper limit, beyond which observation is not possible in practice and beyond which increasing the flow rate has virtually no influence. It remains to be noted that regulating $\dot{m}_J$ is not the preferred choice for exothermic reactions in jacketed tanks, as heating and cooling has to be provided. The manipulated variable of choice is thus the inlet temperature at an optimal flow rate of coolant.

It would appear to be the case that an optimal flow rate in the jacket exists above which its increase only results in an infinitesimally small increase in heat removed. Assuming a tank is cooled and T_R is constant (i.e., in infinitely large

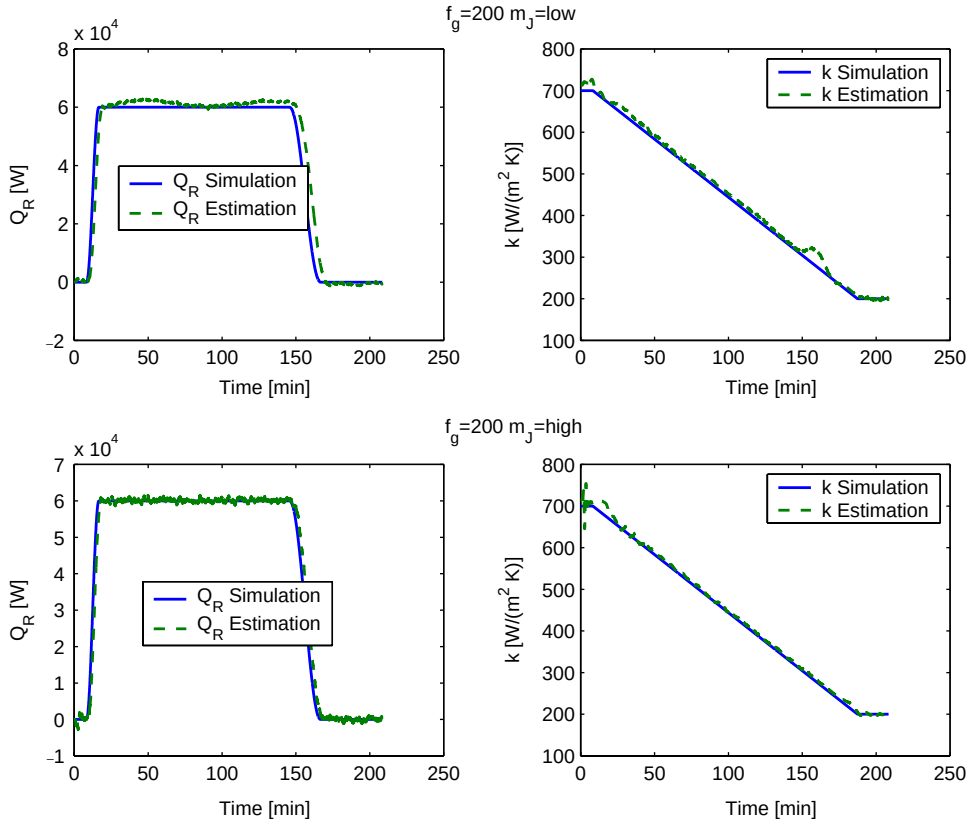

Fig. 8. Simulation of and estimation a $2\,m^3$ reactor with low (top line) and high (bottom line) jacket mass flow rates and a discretised jacket model. Note the improvement over Fig. 7.

tank), an analytical solution can be found for both jacket descriptions.

For the CSTR-jacket the solution becomes:

$$T = \frac{\dot{m}_J c_p T_{J,\mathrm{in}} + kAT_R}{\dot{m}_J c_p + kA} + \frac{\dot{m}_J c_p (T_0 - T_{J,\mathrm{in}}) + kA(T_{J,0} - T_R)}{\dot{m}_J c_p + kA} \times \exp\left(-\frac{1}{m_J c_p}(\dot{m}_J c_p + kA)t\right) \tag{40}$$

for the initial condition

$$T_J(t=0) = T_{J,0}. \tag{41}$$

The solution for the PFR-jacket can be written as

$$T(x) = \begin{cases} T_R - (T_R - T_{J,x_0}) \exp\left(-\dfrac{k}{b\rho c_p} t\right) & t < \frac{x}{v}, \\ T_R - (T_R - T_{J,\mathrm{in}}) \exp\left(-\dfrac{k}{b\rho c_p v} x\right) & t \leqslant \frac{x}{v}. \end{cases} \tag{42}$$

For simplicity and for the sake of the argument, the steady state case for the CSTR-jacket is considered. The aim is to achieve maximum heat removal through the jacket. The equation for the heat removal can be written as

$$\dot{Q}_{\mathrm{out}} = \dot{m}_J c_p (T_{J,\mathrm{out}} - T_{J,\mathrm{in}}) \tag{43}$$

$$\text{with} \quad T_{J,\mathrm{out}} = \frac{\dot{m}_J c_p T_{J,\mathrm{in}} + kAT_R}{\dot{m}_J c_p + kA}. \tag{44}$$

It can be shown easily that the function is monotonously increasing for all $\dot{m}_J > 0$. This means that maximum heat removal rate will be at $\dot{m}_J \to \infty$. As

$$\lim_{\dot{m}_J \to \infty} \dot{Q}_{\mathrm{out}} = kA(T_R - T_{J,\mathrm{in}}) \tag{45}$$

this maximum exists and fractions thereof exist as well.

It would now be possible to include the estimation quality and the heat removal into one objective function and solve an optimization problem. However, it is still up to the user to define the importance of the estimation over the heat removal rate. It seems therefore more appropriate to define some guidelines on how to set $\dot{m}_J$.

There will be a maximum $\dot{m}_J$ defined by the plant itself. This can be used to calculate the fraction of the maximum that can actually be achieved. Furthermore, it should be considered that from

$$\dot{m}_J \to \infty \quad \Rightarrow \quad T_{J,\mathrm{in}} = T_{J,\mathrm{out}}, \tag{46}$$

which means any heat balance calorimetry is impossible as $T_{J,\text{out}}$ only depends on the changes of $T_{J,\text{in}}$ and thus the jacket balance equation ceases to exist. Then, k needs to be known to estimate $\dot{Q}_R$ correctly but cannot be estimated.

It thus seems sensible to consider the following:

- A certain fraction of the maximum heat removal has to be maintained, as it governs the batch time, we suggest 0.9.
- This fraction should allow for a reasonable temperature difference between $T_{J,\text{in}}$ and $T_{J,\text{out}}$.
- In order to calculate this fraction, a good estimation of k is needed, which should be calculated at the beginning of the reaction using a low mass flow rate. To avoid a sudden change in k, $\dot{m}_J$ should guarantee a turbulent regime in the jacket.

If the fraction considered is called φ the jacket flow rate can be calculated in steady state as follows:

$$\dot{m}_J = \frac{\varphi}{1-\varphi}\frac{kA}{c_{p,J}}. \tag{47}$$

For the case of the PFR-jacket the behaviour is analysed differently. The steps are the same as above therefore the explanations are omitted.

$$\dot{Q}_{\text{out}} = \dot{m}_J c_p (T_{J,\text{out}} - T_{J,\text{in}}) \tag{48}$$

$$\text{with} \quad T_{J,\text{out}} = T_R - (T_R - T_{\text{in}}) \exp\left(-\frac{k}{b\rho c_{p,J} v} L\right) \tag{49}$$

$$\text{and} \quad v = \frac{\dot{m}_J}{bh\rho} \tag{50}$$

$$\Rightarrow \lim_{\dot{m}\to\infty} \dot{Q}_{\text{out}} = khL(T_R - T_{J,\text{in}}), \tag{51}$$

$$\Rightarrow \; 0 = \dot{m}_J c_{p,J}\left(T_R - (T_R - T_{J,\text{in}}) \exp\left(\frac{-khL}{c_{p,J}\dot{m}_J}\right) \times -T_{J,\text{in}}\right) - \varphi khL(T_R - T_{J,\text{in}}). \tag{52}$$

For this case $\dot{m}_J$ has to be found numerically from Eq. (52).

The two results yield different values for $\dot{m}_J$ whereby the PFR case requires a lower $\dot{m}_J$ for the same fraction of the maximum cooling capacity.

6.2. Additional sensor placement

If additional temperature sensors are placed on a process, they are normally placed inside the reactor to identify possible hot spots resulting from poor mixing. While this is a valid consideration, we think for calorimetric estimation, additional sensors could also be placed inside the jacket. These sensors can help with two important points when using calorimetry:

1. They can be used to determine the jacket behaviour, estimate the jacket geometry and improve model fitting.
2. When the model is successfully fitted, it will improve the estimation quality.

The additional jacket sensors will improve estimation quality for both cases, for the case the jacket behave like a CSTR as well as for the case the jacket behaves like a PFR. In the first case, it can be treated as a second measurement of the same value $T_{J,\text{out}}$, with which the standard deviation of the random measurement error is reduced. For the second case, the measurement provides additional information about the jacket behaviour.

When the placement of only one additional jacket sensor is considered, the ever changing volume in the tank for the case of a semi-batch reactor has to be taken into account. The most sensible would be to place the sensor in the first half of the considered jacket channel. If the semi-batch reactor is, for example, half full to start with, a sensor placed on half the channel length of the considered channel at that point of operation will move to a quarter the length when the reactor is completely filled.

When collocation is used, calculation is easier, if the sensors are placed on the collocation points. As the liquid level in the tank increases, the collocation points shift, whereas the sensor cannot. Maintaining the collocation point position decreases the discretisation accuracy, as their placement is optimal for the given task. It is thus necessary to calculate the polynomial describing the temperature along the length coordinate and include it into the measurement function.

6.3. Separation of the jacket into PFR and CSTR

Not all jackets of jacketed tank reactors behave like either ideal CSTRs or PFRs. Consider a jacket which does follow the walls of the tank but not the Klöpperform[1] base of the tank. For the Klöpperform base, the jacket will behave like a CSTR, for the rest like a PFR. When the above models are considered, it is possible to combine them to suit this system or any other.

For the above example, the jacket input temperature is the input to a CSTR of the volume around the Klöpperform base. The exit temperature is the inlet temperature to the PFR-model of the jacket. The outlet of that part is the inlet to the PFR-part for which there is no conductive heat transfer. The outlet of that part is the jacket outlet temperature.

Obviously, to fit the model to such a system, temperature sensors in the jacket would be very helpful.

7. Simulation study III

Using the above described extension to the measurement function, an estimation of k and $\dot{Q}_R$ is performed using an extra temperature sensor. Considered is a batch reaction where the extra temperature sensor is placed at half the

[1] Klöpperform is a generally agreed technical term for the specifically ellipsoid base of tank reactors.

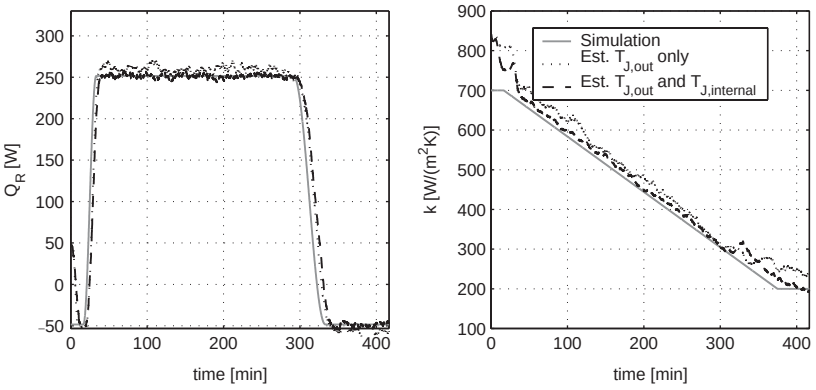

Fig. 9. Comparison of the estimation using the jacket outlet temperature only with the estimation using an additional measurement at half the jacket channel length.

length of the considered jacket channel. The point coincides with a collocation point. The simulation was performed using five collocation points, the estimation uses three.

It can be seen that the estimation using the extra measurement compensates the initial condition error much faster and remains closer to the real value than the estimation using one measurement. The exact same weighting matrices were applied. It is thus possible to tune the filter with the extra measurement less aggressively and achieve a smoother estimate with either equivalent or better accuracy (Fig. 9).

8. Discussion and conclusions

We have demonstrated that the heat of reaction and the heat transfer coefficient for a batch, semi-batch or continuous stirred tank reactor can be estimated using an EKF. We have furthermore shown that the jacket geometry has a major impact on the estimation of the heat transfer coefficient.

Firstly, it can be seen that the EKF performs well for small reactor sizes, even though a plant model mismatch exists between the real plant, where the jacket behaves more like a plug-flow reactor, and the EKF model.

Nonetheless, careful tuning of the filter is paramount. The jacket flow rate has a strong influence on the quality of the observation. An adaptation of the tuning matrix $\mathbf{Q}$ to compensate the jacket flow rate influence was shown. A trade-off between good observer performance and maximum heat removal has to be made, i.e., it might be sensible in the plant to reduce the jacket medium temperature, rather than increase the flow rate. The large amplification necessary also decreases the filtering effect of the EKF.

The model assumption of an ideally stirred jacket is reasonable for state estimation only if the reactor size is small. However, it becomes obvious for larger reactors that estimation quality decreases considerably with reactor size.

Secondly, we developed a model extension to include the case in which the reactor jacket behaves like a PFR. It is achieved by applying orthogonal collocation to the partial differential equation describing the jacket temperature. Even for a small number of collocation points, the results are very good.

Thirdly, a direct extension of the considered jacket behaviour onto adding measuring sensors to the system was performed. If the jacket behaves like a PFR, an additional measurement in the jacket improves the estimation quality and provides an inside into the real channel geometry. It can also be used well in calibration and model fitting.

Finally, as higher mass flow rates in the jacket result in a degradation of estimation quality, a practical approach to calculate the lowest sensible jacket flow rate has been presented, which does, however, require an initial estimate of k.

These points show that good model fitting and good estimation will be an iterative process which can be improved with every reaction.

In the practical case, the reactor geometry should be analyzed carefully. The model should then be fitted off line to those conditions. After that, a simple calibration experiment should be run and model fitting needs to be performed. From typical reaction data, model fitting can be enhanced and a first guess of k can be obtained. The minimum sensible mass flow rate needs to be calculated and with typical reaction data the EKF needs to be tuned. These steps should be performed for a few historical batch runs preferably out of a large range of different processes to allow for continuous model fitting and filter tuning improvement.

9. Future work

As indicated in the title, this work considers the theoretical side of the estimation of $\dot{Q}_R$ and k. Following in a future paper, we will describe applications of the state estimation scheme to different reactors of different sizes and geometries.

The future work will therefore cover the following points:

- *Efficient calibration*: An efficient calibration scheme is absolutely necessary to be able to apply the scheme to

different reactors. This will have follow the steps outlined above.

- *Controlled application*: The calibration and state estimation scheme will be applied to well known and studied laboratory and pilot scaled reactors using a defined heat source to test it in real processes.
- *Real life application*: The presented methods will be applied to laboratory and pilot scale reactors running exothermic reactions and subsequently to industrial scale reactors to show the usefulness of the method.

Notation

A	heat transfer area, $0.2\,\mathrm{m}^2$
A_B	base area of the reactor, m^2
$A_{\max}$	maximum heat transfer area, $0.2\,\mathrm{m}^2$
A_X	cross sectional flow area, $hb\,\mathrm{m}^2$
b	channel width, 0.02 m
c_p	fluid heat capacity, 4000 J/kgK
$c_{p,S}$	heat capacity of the reactor wall material, J/kgK
C_R	total absolute heat capacity of the reactor, J/K
d_R	reactor diameter, m
h	channel height, 0.05 m
h_R	level of the reaction medium in the reactor, m
k	heat transfer coefficient, $10\,\mathrm{W/Km}^2$
L	maximum length of the location coordinate, $\frac{A}{h}$ m
m_J	mass in the jacket, $Ab\rho$ kg
$\dot{m}_J$	mass flow through the jacket, 0.05 kg/s
m_S	mass of the reactor wall, kg
p	number of collocation points,
$\dot{q}_{J,\mathrm{loss}}$	heat loss from the jacket in one channel element, W
$\dot{Q}_{J,\mathrm{in}}$	heat flow into the jacket, W
$\dot{Q}_{J,\mathrm{out}}$	heat flow out of the jacket, W
$\dot{Q}_J$	conductiveheat flow through reactor wall, W
$\dot{Q}_{J,\mathrm{loss}}$	heat loss from the jacket, W
$\dot{Q}_{R,\mathrm{in}}$	heat flow of the feed, W
$\dot{Q}_{R,\mathrm{loss}}$	heat loss of the reactor, W
$\dot{Q}_{R,\mathrm{out}}$	heat flow out of the reactor, W
$\dot{Q}_{R,\mathrm{source}}$	heat of reaction, W
$T_{J,\mathrm{in}}$	jacket inlet temperature, K
T_J	temperature in the jacket, K
$T_{J,U}$	temperature in the upper jacket part, K
$T_{J,L}$	temperature in the lower jacket part, K
$T_{J,\mathrm{out}}$	jacket outlet temperature, K
T_{J,z_0}	initial temperature along the z coordinate, K
$T_{J,0}$	initial temperature at $t=0$, K
T_R	temperature in the reactor, K
v	fluid velocity, $\frac{\dot{m}}{\rho hb}$ m/s
$\dot{V}_{R,\mathrm{in}}$	inlet flow to the reactor, m^3/s
$\dot{V}_{R,\mathrm{out}}$	outlet flow of the reactor, m^3/s
$\hat{\mathbf{x}}_{k\|j}$	estimated state vector at time t_k based on measurements up to time t_j
z	distribution coordinate, m
z_i	ith collocation point,

Greek Letter

ρ	fluid density, $1000\,\mathrm{kg/m}^3$

Acknowledgements

Both authors formerly worked at the Chair of Process Control, University of Dortmund, Germany. The financial support of Stefan Krämer by the Deutsche Forschungsgemeinschaft (project EN 152/31-1) during his work in Dortmund and by the Marie Curie Fellowship (Contract HPMT-CT-2001-00227) during a stay at the Institute for Polymer Materials (POLYMAT) at the University of the Basque Country is gratefully acknowledged.

The authors also thank Prof. Asua of the Institute for Polymer Materials (POLYMAT) at the University of the Basque Country and Prof. Engell, Chair of Process Control, University of Dortmund, Germany for helpful discussions. Furthermore, the discussion and help of the student Gerit Niggemann is very much appreciated.

Appendix A. Detailed development of the PFR jacket equations

The jacket is unravelled and approximated by a rectangular flow channel, one side of which is used for convective heat transfer. The problem is modelled by looking at one channel element x to $x+\mathrm{d}x$ as shown below:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \dot{Q}_{\mathrm{conv},x} - \dot{Q}_{\mathrm{conv},x+\mathrm{d}x} + \dot{Q}_J$$

$$\text{with} \quad \dot{Q} = mc_p \frac{\partial T_J(t,x)}{\partial t},$$

$$\dot{Q}_{\mathrm{conv},x} = \dot{m}c_p T_J(t,x),$$

$$\dot{Q}_{\mathrm{conv},x+\mathrm{d}x} = \dot{m}c_p T_J(t,x) + \dot{m}c_p \frac{\partial T_J(t,x)}{\partial x}\,\mathrm{d}x,$$

$$\dot{Q}_J = kA(T_R - T_J(t,x)).$$

$$\Rightarrow \quad mc_p \frac{\partial T_J(t,x)}{\partial t} = \dot{m}c_p T_J(t,x) - \dot{m}c_p T_J(t,x) - \dot{m}c_p \frac{\partial T_J(t,x)}{\partial x}\,\mathrm{d}x + kA(T_R - T_J(t,x)),$$

$$hb\rho c_p \mathrm{d}x \frac{\partial T_J(t,x)}{\partial t} = -vhb\rho c_p \frac{\partial T_J(t,x)}{\partial x}\,\mathrm{d}x + kh\mathrm{d}x(T_R - T_J(t,x)),$$

$$\frac{\partial T_J(t,x)}{\partial t} = -v\frac{\partial T_J(t,x)}{\partial x} + \frac{k}{b\rho c_p}(T_R - T_J(t,x)). \quad \text{(A.1)}$$

Appendix B. Geometry factor

The models are extended by a geometry factor (f_G), whereby the ratio between the vessel radius and height is kept.

B.1. CSTR model

For the CSTR model presented in Eqs. (1)–(4) the geometry factor should increase the volume by the desired factor, i.e., $V = f_G V_S$. This leads to

$$r_R = \sqrt[3]{f_G} r_{R,S}, \tag{B.2}$$

$$b = \sqrt[3]{f_G} b_S, \tag{B.3}$$

$$\dot{Q}_{R,\text{source}} = \underbrace{\dot{q}_{R,\text{source}}}_{[\frac{W}{l}]} h_R A_B, \tag{B.4}$$

$$\dot{Q}_{R,\text{loss}} = \underbrace{\dot{q}_{R,\text{loss}}}_{[\frac{W}{l}]} A, \tag{B.5}$$

for the geometric sizes and to

$$h_{R,0} = \sqrt[3]{f_G} h_{R,0,S}, \tag{B.6}$$

$$\dot{m} = \sqrt[3]{f_G^2} f_{PFR} \dot{m}_S, \tag{B.7}$$

$$\dot{V}_{R,\text{in}} = f_G \dot{V}_{R,\text{in},S}, \tag{B.8}$$

$$\dot{V}_{R,\text{out}} = f_G \dot{V}_{R,\text{out},S}, \tag{B.9}$$

for initial conditions and manipulated variables, where S denotes the standard value. For a CSTR, f_{PFR} will be 1, for an explanation of this value, see below.

If Eqs. (B.2)–(B.9) are inserted into the CSTR equations, the following results:

$$\pi r_{R,S}^2 \sqrt[3]{f_G^2} \frac{\mathrm{d}h_R}{\mathrm{d}t} = f_G(\dot{V}_{R,\text{in},S} - \dot{V}_{R,\text{out},S})$$

$$\begin{aligned}\pi r_{R,S}^2 h_R \sqrt[3]{f_G^2} \frac{\mathrm{d}T_R}{\mathrm{d}t} &= \frac{1}{\rho_R c_{p,R}} \Bigg(\rho_R c_{p,R} f_G \dot{V}_{R,\text{in},S}(T_{R,\text{in}} - T_R) \\ &+ \dot{q}_{R,\text{source}} h_R \pi r_{R,S}^2 \sqrt[3]{f_G^2} \\ &- \dot{q}_{R,\text{loss}} \left(\pi r_{R,S}^2 \sqrt[3]{f_G^2} + 2\pi r_{R,S} h_R \sqrt[3]{f_G} \right) \\ &- k \left(\pi r_{R,S}^2 \sqrt[3]{f_G^2} + 2\pi r_{R,S} h_R \sqrt[3]{f_G} \right) (T_R - T_J) \Bigg),\end{aligned} \tag{B.10}$$

$$\begin{aligned}\frac{\mathrm{d}T_J}{\mathrm{d}t} &= \frac{1}{f_G m_S c_p} \Bigg(\sqrt[2]{f_G} \dot{m}_S c_p (T_{J,\text{in}} - T_J) \\ &+ k \left(\pi r_{R,S}^2 \sqrt[3]{f_G^2} + 2\pi r_{R,S} h_R \sqrt[3]{f_G} \right) (T_R - T_J) \Bigg).\end{aligned} \tag{B.11}$$

Divide Eqs. (B.10) and (B.11) by $\sqrt[3]{f_G^2}$ and it becomes obvious, what the geometry factor influences:

$$\frac{\mathrm{d}h_R}{\mathrm{d}t} = \frac{\sqrt[3]{f_G}}{\pi r_{R,S}^2} (\dot{V}_{R,\text{in},S} - \dot{V}_{R,\text{out},S}) \tag{B.12}$$

$$\begin{aligned}\frac{\mathrm{d}T_R}{\mathrm{d}t} &= \frac{\dot{V}_{R,\text{in},S}}{\pi r_{R,S}^2 h_R} \sqrt[3]{f_G} (T_{R,\text{in}} - T_R) \\ &+ \frac{1}{\rho_R c_{p,R}} \Bigg(\dot{q}_{R,\text{source}} - \left(\frac{1}{h_R} + \frac{2}{r_{R,S}} \sqrt[3]{f_G^{-1}} \right) \dot{q}_{R,\text{loss}} \\ &- k \left(\frac{1}{h_R} + \frac{2}{r_{R,S}} \sqrt[3]{f_G^{-1}} \right) (T_R - T_J) \Bigg),\end{aligned} \tag{B.13}$$

$$\begin{aligned}\frac{\mathrm{d}T_J}{\mathrm{d}t} &= \frac{1}{m_S c_p} \Bigg(\sqrt[3]{f_G^{-1}} \dot{m}_S c_p (T_{J,\text{in}} - T_J) + k \Bigg(\sqrt[3]{f_G^{-1}} r_{R,S}^2 \\ &+ 2\pi \sqrt[3]{f_G^{-2}} r_{R,S} h_R \Bigg) (T_R - T_J) \Bigg).\end{aligned} \tag{B.14}$$

The initial condition for h_R is also multiplied by $\sqrt[3]{f_G}$.

B.2. PFR model

For the PFR model the influences are the same.

However, it is questionable if the channel height in a real reactor would remain the same or is adjusted accordingly. The factor to keep it at the same level here, would be the velocity v. Therefore, a second design factor or relating constant is included to relate the mass flow and the channel height, f_{PFR}.

If the channel height is increased by $\sqrt[3]{f_G}$, it means the ratio of vessel height to channel height remains the same, i.e., the length (L), one plug has to travel is increased by $\sqrt[3]{f_G}$. As such, the mass flow would have to be decreased by $\sqrt[3]{f_G}$ to maintain velocity. Therefore the following relations is added:

$$h = \sqrt[3]{f_G} f_{\text{PFR}} h_S. \tag{B.15}$$

A sensible value is 1 as the velocity remains the same. The largest possible value is $\frac{h_J}{h_S}$ where h_J denotes the height of the wall covered by the jacket.

References

Bartanek, B., Gottfried, M., Korfhage, K., Pauer, W., Schulz, K., Moritz, H.-U., 1999. Closed loop control of chemical composition in free radical copolymerization by online reaction monitoring via calorimetry and IR-Spectroscopy. In: RC User Forum Europe. pp. 1–13.

BenAmor, S., Colombie, D., McKenna, T., 2002. Online reaction calorimetry. Application to the monitoring of emulsion polymerization without samples or models of the heat transfer coefficient. Industrial Engineering Chemical Research 41, 4233–4241.

Birk, J., 1992. Rechnergestützte Analyse und Lösung nichtlinearer Beobachtungsaufgaben. No. 294 in Fortschrittsberichte. VDI-Verlag GmbH, Düsseldorf.

Carloff, R., Proß, A., Reichert, K.-H., 1994. Temperature oscillation calorimetry in stirred tank reactors with variable heat transfer. Chemical Engineering Technology 17, 406–413.

de Buruaga, I.S., Echevarria, A., Armitage, P.D., de la Cal, J.C., Leiza, J.R., Asua, J.M., 1997. On-line control of a semibatch emulsion polymerization reactor based on calorimetry. A.I.Ch.E. Journal 43 (4), 1069–1081.

Fevotte, G., McKenna, T.F., Othman, S., Santos, A.M., 1998. A combined hardware/software sensing approach for on-line control of emulsion polymerisation processes. Computers & Chemical Engineering 22 (SS), S443–S449.

Franke, M., 2000. Kalorimetrische Berechnung des Monomerverbrauchs einer Emulsionscopolymerisation mit zwei Monomeren. Master's Thesis, Universität Dortmund, Fachbereich Chemietechnik.

Freire, F.B., McKenna, T.F., Othman, S., Guidici, R., 2004. A new approach to the joined estimation of the heat generated by a semicontinuous emulsion polymerization Q_R and the overall heat exchange parameter UA. Brazilian Journal of Chemical Engineering 21 (2), 293–305.

Gelb, A., 1974. Applied Optimal Estimation. The MIT Press, Massachusetts Institute of Technology,

Georgakis, C., Aris, R., Amundson, N.R., 1977. Studies in the control of tubular reactors. Chemical Engineering Science 32, 1359–1369.

Gesthuisen, R., Engell, S., 2000. State estimation for tubular reactors with measurements at the outlet only. In: Proceedings of ADCHEM 2000, International Symposium on Advanced Control of Chemical Processes, vol. 2. ADCHEM, Pisa, Italy, June 14–16.

Gugliotta, L.M., Arotcarena, M., Leiza, J.R., Asua, J.M., 1995. Estimation of conversion and copolymer composition in semicontinuous emulsion polymerization using calorimetric data. Polymer 36 (10), 2019–2023.

Guo, B., Jiang, A., Hua, X., Jutan, A., 2001. Nonlinear adaptive control for multivariable chemical processes. Chemical Engineering Science 56, 6781–6791.

Jazwinski, A., 1970. Stochastic Processes and Filtering Theory. Academic Press, New York, London.

Krämer, S., Franke, M., Gesthuisen, R., 2001. Online monitoring of semicontinuous emulsion copolymerization: comparing Extended Kalman filtering to feed-forward calorimetry. In: Kollár, I. (Ed.), Conference Proceedings of the Instrumentation and Measurement Technology Conference. IEEE, pp. 931–936.

Krämer, S., Gesthuisen, R., Engell, S., 2003a. Fehlerhafte Schätzung des Wärmeübergangskoeffizienten in Rührkesseln durch Modellvereinfachung. In: GMA-Kongress–Automation und Information in Wirtschaft und Gesellschaft. vol. 1756 of VDI-Bericht. VDI-GMA, VDI-Verlag, Düsseldorf, GMA-Kongress 2003, Baden-Baden, 3–4 June 2003, pp. 529–536.

Krämer, S., Gesthuisen, R., Engell, S., Asua, J.M., 2003b. Simultaneous estimation of heat transfer coefficient and reaction heat in semibatch processes. In: Bequette, B.W. (Ed.), Conference Proceedings of the American Control Conference 2003. American Automatic Control Council, Denver, USA, pp. 1980–1981.

Luca, P.G.D., Scali, C., 2002. Temperature oscillation calorimetry: robustness analysis of different algorithms for the evaluation of the heat transfer coefficient. Chemical Engineering Science 57, 2077–2087.

McKenna, T.F., Fevotte, G., Graillat, C., Guillot, J., 1996. Joint use of calorimetry, densimetry and mathematical modelling for multiple component polymerizations. Trans IChemE 74, 340–348.

McKenna, T.F., Othman, S., Févotte, G., Santos, A.M., Hammouri, H., 2000. An integrated approach to polymer reaction engineering: a review of calorimetry and state estimation. Polymer Reaction Engineering 8 (1), 1–38.

Othman, N., Santos, A.M., Févotte, G., McKenna, T., 2002. Monitoring of emulsion polymerizations: a study of reaction kinetics in the presence of secondary nucleation. The Canadian Journal of Chemical Engineering 80, 88–104.

Santos, A., Bentes-Freire, F., BenAmor, S., Pinto, J.C., Guidici, R., McKenna, T.F., 2001. On-line monitoring of emulsion polymerization: conductivity and "cascade" calorimetry. Dechema Monographs, vol. 137, pp. 609–615.

Schmidt, C.-U., Reichert, K.-H., 1988. Reaction calorimeter—a contribution to safe operation of exothermic polymerisations. Chemical Engineering Science 43 (8), 2133–2137.

Tauer, K., Müller, H., Schellenberg, C., Rosengarten, L., 1999. Evaluation of heterophase polymerizations by means of reaction calorimetry. Colloids and Surfaces A 153, 143–151.

Tietze, A., Proß, A., Reichert, K.H., 1995. Temperature oscillation calorimetry in stirred tank polymerization reactors. In: Reichert, K.H. (Ed.), Fifth International Workshop on Polymer Reaction Engineering. Dechema Monographien, VCH-Verlagsgesellschaft, Berlin, pp. 673–681.

Tietze, A., Lüdtke, I., Reichert, K.-H., 1996a. Temperature oscillation calorimetry in stirred tank reactors. Chemical Engineering Science 51 (11), 3131–3137.

Tietze, A., Pross, A., Reichert, K.-H., 1996b. Temperaturschwingungskalorimetrie in Rührkesselreaktoren. Chemie Ingenieur Technik 1+2, 97–100.

Vicente, M., Amor, S.B., Gugliotta, L.M., Leiza, J.R., Asua, J.M., 2001. Control of molecular weight distribution in emulsion polymerization using on-line reaction calorimetry. Industrial and Engineering Chemistry Research 40 (1), 218–227.

Villadsen, J., Michelsen, M., 1978. Solution of Differential Equation Models by Polynomial Approximation. Prentice-Hall, Englewood Cliffs.

Walcott, B.L., Corless, M.J., Zak, S.H., 1987. Comparative study of nonlinear state-observation techniques. International Journal of Control 45 (6), 2109–2132.

Weber, H., 1974. Isothermal calorimetry for thermodynamic and kinetic measurement. Ph.D. Thesis, ETH Zürich, Zürich.