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ADVANCED ON-LINE DATA TREATMENT FOR A BENCH SCALE HEAT FLOW CALORIMETER

L.G. Karlsen, H. Søeberg and J. Villadsen
Instituttet for Kemiteknik
Danmarks Tekniske Højskole, Lyngby (Denmark)

ABSTRACT

Reduction of response time and minimization of base line drift are major issues in the development of software for microprocessor controlled analytical instruments. We present a nearly optimal data treatment system for the bench scale heat flow calorimeter which is used to study chemical kinetics through continuous measurement of the heat flow from the calorimeter-reactor.

Kinetic and thermodynamic parameters are estimated by a fast, and still low-variance procedure, also for quite fast reactions with a time constant down to 200 s. A variation of the reactor side heat transfer coefficient h_R during the progress of the chemical reaction is also estimated on line, simultaneously with the thermokinetic parameters.

INTRODUCTION

Lately the design of several bench scale calorimeters and the accompanying data treatment methods have been described in the literature (refs. 1-4 and refs. 1-5 of ref. 5). We study the BSC81, developed by Ciba-Geigy (ref.5). The reactor is a jacketed 2.5 liter glass vessel with a calorimeter time constant τ_C and a reactor wall heat conduction time constant τ_W:

$$\tau_C = \frac{m_R C_{PR}}{UA} = 800 \text{ s (water) and } \quad \tau_W = \frac{L^2 \rho_W C_{PW}}{\lambda_W} = 25 \text{ s.}$$

Our main goal is to develop software for accurate measurement of the differential heat evolution q as well as the total heat Q which is evolved up to a certain conversion or to completion of the reaction. The measurements should be valid also for: a) Reactions which are fast compared to the calorimeter time constant τ_C. b) A heat flux which is changing rapidly compared to the wall time constant τ_W. c) A time varying reactor side heat transfer coefficient h_R. d) Changes of up to 20°C in the reactor temperature T_R within the single experiment (e.g. thermal initiation or test of stability).

a) and b) are concerned with the response time of the calorimeter, while c) and d) deal with what normally is referred to as base line drift.

DESCRIPTION OF THE PROCEDURE

The fundamental calorimeter equation is

$$m_R C_{PR} \frac{dT_R}{dt} = q_F\ (h_J, \tau_W, h_R) + q_{sec} + q_c + q \qquad (1)$$

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The heat flux q_F from the reactor wall depends on the heat transfer properties (h_J, τ_W, h_R) through the solution of the reactor wall heat conduction problem. The secondary heat effect q_{sec} arises mainly from heat loss to the surroundings and from impeller heat dissipation.

We shall assume that $h_J(T_J)$, $h_R(T_{R,\ t=0})$, $m_R C_{PR}$ and $q_{sec}(T_R, T_S)$ have been found by the calibration procedure of ref. 5 before the start of the kinetic experiment at t=0. For t>0 we estimate the differential heat of reaction (and a heat of mixing), q(t) using measurements of T_R, T_J and T_S and a Reduced Order Estimator (a so-called Luenberger Observer) as described theoretically in ref. 5. In this paper we shall denote an estimator working on (1) as our Primary Estimator.

When h_R varies with time (e.g. with the extent of the reaction) we let the primary estimator alternate between estimation of q and h_R. The calibration heat input q_C is switched off when we estimate q and on when h_R is estimated.

As a result of the primary q-estimation we obtain a time series $\hat{q}_k$ from which a recursive time series model (eq. 2) for q at the actual level of h_R (= h_{R0}) is determined. Additionally, we determine a model (eq. 3) for the sensitivity $\nabla\bar{q}$ of the prediction $\bar{q}$ with respect to h_R from the measurements of ∇q, which is defined by eq. (4).

$$\bar{q}_{k+1}(h_{R0}) = (1-\Theta_1)\bar{q}_k(h_{R0}) + \Theta_2 \tag{2}$$

$$\nabla\bar{q}_{k+1}(h_{R0}) = (1-\Theta_3)\nabla\bar{q}_k(h_{R0}) + \Theta_4 \tag{3}$$

$$\nabla q = \frac{\partial q}{\partial h_R} = -\frac{\partial q_F}{\partial h_R} \approx \frac{\partial}{\partial h_R} \{A(\frac{1}{h_R} + \frac{L}{\lambda_W} + \frac{1}{h_J})^{-1} (T_R - T_J)\} \tag{4}$$

The second equality in (4) $(\frac{\partial q}{\partial h_R} = -\frac{\partial q_F}{\partial h_R})$ originates from (1) where q_F is the only h_R-dependent term. The approximate expression in (4) is valid for temperature variations that are slow compared to τ_W.

The parameters Θ_1 to Θ_4 are determined by filtering the time series for $\hat{q}$ and ∇q through the models (2) and (3) to obtain prediction errors $\varepsilon_q = \hat{q} - \bar{q}$ and $\varepsilon_{\nabla q} = \nabla q - \nabla\bar{q}$. These are used in parameter estimation algorithms which achieve a Gauss-Newton minimization of the prediction errors. The computational procedure (ref. 21 of ref. 5) results in response times for the parameter estimates and variances of the predictions $\bar{q}$ and $\nabla\bar{q}$ which are independent of the prediction error sensitivity w.r.t. Θ_1 to Θ_4. This is advantageous since these sensitivities are nearly proportional to q and therefore strongly varying during the chemical reaction. We denote the estimators which work on models (2) and (3) our Secondary Estimators.

During the primary h_R-estimation we predict q by a two term Taylor expansion:

$$\bar{q}_k(h_R) \approx \bar{q}_k(h_{R0}) + \nabla\bar{q}_k(h_{R0})(h_R - h_{R0}) \qquad (5)$$

where $\bar{q}_k(h_{R0})$ and $\nabla\bar{q}_k(h_{R0})$ are obtained from the identified models (2) and (3).

Figure 1 shows the flow of information in our two-tier data treatment system for BSC81.

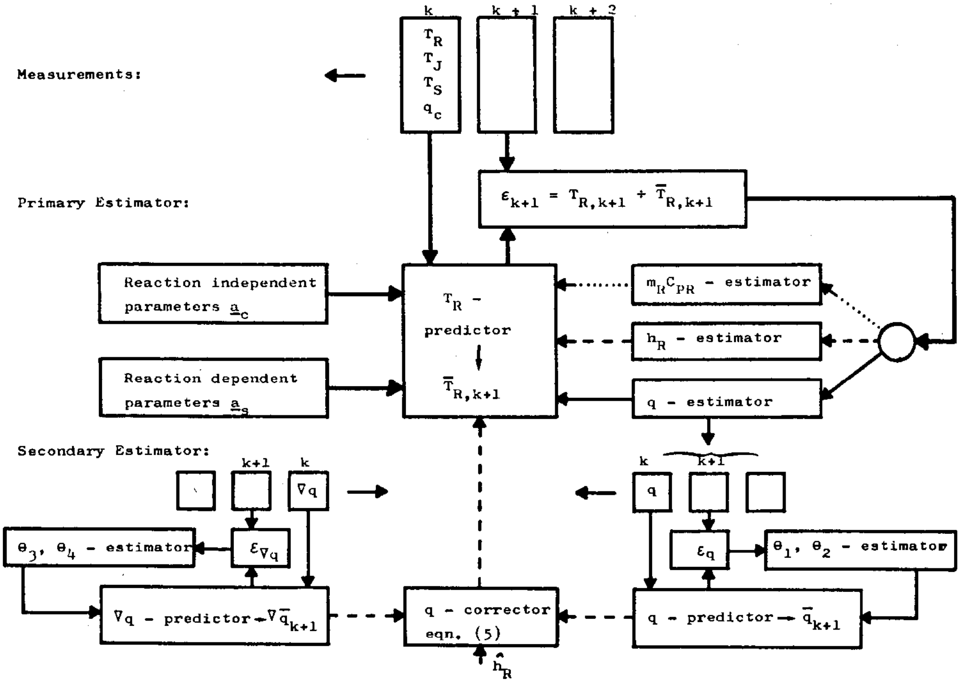

Fig. 1. Information flow diagram. The T_R-predictor is based on (1) and on a two point collocation solution of the reactor wall heat conduction problem with correct integration of the resulting DE's (ref. 16 of ref. 5). The time increment Δ between sampling time k and k+1 is 2 s. Memory area: 5 K words. Active information flows: ——▶ always open. ·····▶ $m_R C_{PR}$-estimation. - - -▶ h_R-estimation. ——▶ Estimation of q and Θ_1-Θ_4.

TEST CONDITIONS

To test the procedure we have constructed an experiment in which we are able to control h_R and simulate q. The reactor contains 2.0 litres glycerol well stirred by a turbine at 350 min^{-1}. By controlling T_R within [50; 75] °C we obtain h_R values that vary from 464 to 746 Wm^{-2} K^{-1}.

In this range the ratio between reactor side and overall heat transfer resistance h_R^{-1}/U^{-1} varies between 29% and 22%, and consequently h_R has a significant influence on U ($135 < U < 160$ Wm^{-2} K^{-1}).

A q(t)-function is simulated by subtracting $q_t(t)$ from the q-input to the T_R-predictor of Fig. 1. If the reactor model is correct the primary q-estimator estimates $\hat{q}(t)$ equal to $q_t(t)$, but superimposed by noise that originates from the T_R-measurements. However, any model error in the T_R predictor will show up as an error in $\hat{q}(t)$.

RESULTS

We show two examples: In Fig. 2 h_R is constant and the kinetics of the first order reaction is estimated. In Fig. 3 both h_R and the kinetic parameter are estimated.

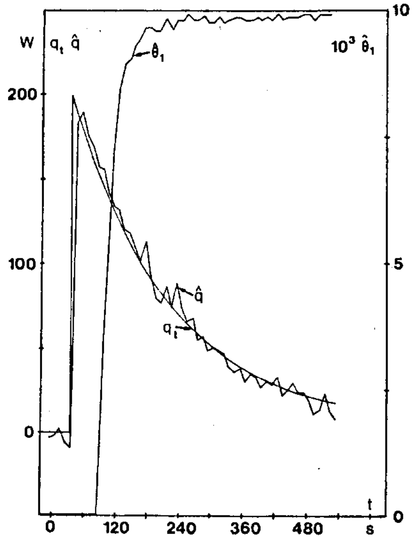

Fig. 2. Response of data treatment system estimating q and Θ_1 for a first order reaction. The true rate constant $k = 5 \cdot 10^{-3}$ s^{-1}, ($\Theta_1 = 1-\exp(-k\Delta) = 10^{-2}$). The true q response q_t and every fifth estimate of q ($\hat{q}$ from the primary estimator) and of Θ_1 ($\hat{\Theta}_1$ from the secondary estimator) are shown.

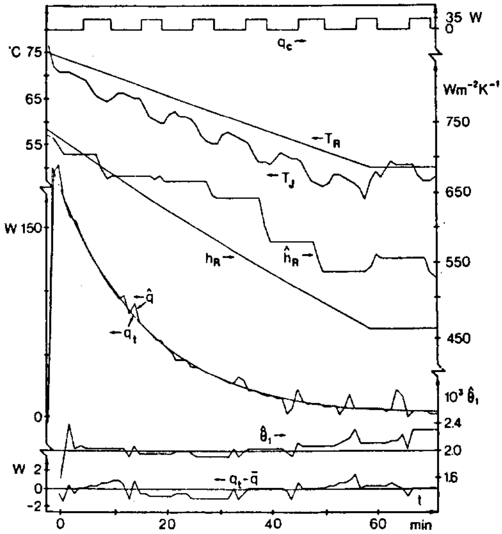

Fig. 3. Alternating q/h_R estimation. T_R decreases linearly from 75°C to 50°C in 60 minutes. This leads to a nearly linear h_R(true)-gradient of -4.7 Wm^{-2} K^{-1} min^{-1}. Simultaneously we simulate a 1. order reaction with $\tau_R = 1/k = 16.7$ min and $q_t^{\circ} = 200$ W. The heat flux $-q_F$ is within [30; 70] W.

The response time (95% level) of the constant h_R estimation of q in Fig. 2 is designed to be less than 6 s, and this is seen to agree with the observed $\hat{q}$-response. The response time of $\hat{\Theta}_1$ is 80 s, and after 170 s $\hat{\Theta}_1$ is correct within 2%.

We see on Fig. 3 that the error level $q_t-\bar{q}$ for the two-level q-estimator stays below 1 W also during the periods where h_R is estimated (and the q-estimator is switched off). This is due to the very good estimation of Θ_1 ($\hat{\Theta}_1$). The estimate $\hat{h}_R$ follows the true variation of h_R quite well, but for T_R decreasing below 55°C the offset of $\hat{h}_R$ increases to 10%. The calorimeter model was calibrated at T_R = 70°C and any unmodelled changes in parameter values which are caused by the large (and in normal operation of the calorimeter unreasonably large) excursions of T_R will lead to an offset in $\hat{h}_R$.

Table 1 lists the results of each estimation cyclus. One cyclus lasts approx. 10 min of which 5 is active estimation time, the remainder is equilibration time after switch on and off of q_c.

During the major part of the experiment $\hat{\Theta}_1$ stays within 4% of its true value, but the accuracy decreases as the chemical reaction fades out and q decreases. This is caused by the decreasing sensitivity of the q-prediction w.r.t. Θ_1 as q decreases to zero. However, the increasing error in $\hat{\Theta}_1$ has no influence on the prediction of q - exactly because the sensitivity of q with respect to Θ_1 decreases when the reaction tends to completion.

The accuracy of $\hat{U}$ and thereby of q_F is within 2.5% for a 16% change in U (from T_R = 75 to 53°C). For the large value $(-q_F)$ = 70 W we have thus succeeded in estimating q_F with an error of ∿1.8 W as compared to an estimation procedure when the variation in h_R was not taken into account (error 11 W).

TABLE 1

Estimation results from Fig. 3. $\hat{\Theta}_1 = 1-\exp(-\hat{k}\Delta)$, Δ = 2s.

$$U = (h_R^{-1} + \frac{L}{\lambda_W} + h_J^{-1})^{-1} = [h_R^{-1} + \frac{4.1}{1100 + 1/2(T_R+T_J)} + (435+3.35\cdot T_J)^{-1}]^{-1}$$

Time	T_R	$\hat{\Theta}_1=1-\exp(-k\Delta)$	$\hat{h}_R$	h_R	$(\hat{U}-U)/U$
min	°C		$Wm^{-2}\ K^{-1}$	$Wm^{-2}\ K^{-1}$	
0	74.9	0	740	746	-0.002
4	73.4	0	712	724	-0.004
12	70.3	0.00205	684	682	0.001
22	66.2	0.00195	673	632	0.015
32	62.1	0.00193	651	588	0.025
42	58.0	0.00203	588	544	0.020
53	53.3	0.00206	545	494	0.027
63	50.2	0.00211	565	464	0.055
73	50.2	0.00232	539	464	0.042

CONCLUSIONS

We draw the following conclusions regarding our present data treatment system for BSC81:

1) We can obtain fast and reliable estimates of kinetic or other thermokinetic parameters of the q-model.

2) We can track h_R-variations in a satisfactory manner if the h_R-gradient is smaller than 5 Wm^{-2} K^{-1} min^{-1}. For larger gradients in h_R the above method is not feasible due to the length of the estimation cyclus. For larger h_R gradients one should account for the h_R-variation by off-line data treatment. Our simulated kinetic experiments were made under circumstances where T_R varied by 25°C. In a normal kinetic experiment T_R varies much less, and the estimation of h_R is likely to be even better since unknown model errors caused by the T_R variation are eliminated.

Thus, in conclusion we may claim that the above described procedure is an important improvement concerning the applicability of BSC81. It is simple to use and leads to accurate estimates of the chemical and physical properties of the reactions and reaction mixture.

NOMENCLATURE

A	Heat transfer area, m^2
h_R	Reactor side heat transfer coefficient
h_J	Jacket side heat transfer coefficient
k	1. order rate constant, s^{-1}
L/λ_W	Wall heat conduction resistance,
$m_R C_{PR}$	Heat capacity, J K^{-1}
Q	Total heat, J
q_F	Heat flux from reactor wall, W
q_C	Calibration heat input, W
q_{sec}	Secondary heat effects, W
q	Reaction heat evolution, W
q_t	True q, W
T_R	Reactor temperature, °C
T_J	Jacket temperature, °C

T_S	Temperature of surroundings, °C
U	Overall heat transfer number
Δ	Sampling period, s
ε_q $\varepsilon_{\nabla q}$	Secondary prediction errors
Θ_1 to Θ_4	Model parameters for $\bar{q}(t)$ and $\nabla\bar{q}(t)$
τ_C	Calorimeter time constant, s
τ_W	Reactor wall time constant, s
τ_R	Reaction time constant 1/k, s
∇q	Sensitivity of q w.r.t. h_R
$\hat{x}$	Primary estimate of x
$\bar{x}$	Secondary prediction of x

Subscript

k	Time index

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