Thermochimica Acta, 236 (1994) 81–91
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01607-5

A bench-scale evaporative calorimeter for diagnostic and control possibilities in vacuum processes

G. Févotte [a],* and J.P. Klein [b]

[a] *Laboratoire de Contrôle des Procédés, CPE-ICPI, 31 Place Bellecour, 69288 Lyon Cedex 02, France*
[b] *Laboratoire d'Automatique et de Génie des Procédés, LAGEP, CNRS URA D1328 et GDR 974, Université Lyon I, 43 Bld. du 11 Nov. 1918, 69622 Villeurbanne Cedex, France*

(Received 2 August 1993; accepted 18 September 1993)

Abstract

For various chemical processes, heat and mass evaporative flows are generated through vacuum control in order to ensure isothermal operations or flexible tracking of temperature trajectories.

To study such processes, a 5-liter bench-scale evaporative calorimeter is presented in this paper. As an example, the application of this microcomputer-controlled calorimeter to the on-line identification of the differential heat evolution during batch evaporative crystallizations is reported. It is shown that satisfactory estimated results are obtained by means of a recursive least-squares policy. These results could allow an extension of diagnostic and control possibilities for many common processes which operate in vacuum conditions.

INTRODUCTION

In research applications and process studies, calorimetric methods have been successfully applied in many fields of chemical processes. Based on energy and mass balance equations, the calorimetric approach has led to significant improvements in the control of numerous and various systems. For polymerization reactors, accurate monitoring and advanced control schemes have been reported [1–3]. For chemical reactions [4–6] or biotechnological processes [7, 8], data and estimates derived from on-line calorimetry allow a fruitful extension of diagnostic and control possibilities. Detection of runaway or of semibatch reactor overfeed [9, 1], assessment of heat transfer and power consumption in stirred tanks [10], and estimations of heat transfer variations [3] are some examples of specific applications that have brought new ideas and tools that could be developed in the field of industrial chemical process control.

---

* Corresponding author.

Among chemical processes, it appears that no specific studies have been reported that consider evaporative processes. This is probably because they are generally encountered at the industrial, rather than the laboratory, level. However, as outlined by Eckles and Benz [11], many common processes in the chemical process industry operate at sub-atmospheric, or vacuum, conditions. For example, vacuum processes offer important advantages when high purities are desired or when stringent temperature conditions are involved. These advantages include lower operating costs and simply the ability to do something that cannot otherwise be accomplished.

This paper describes a bench-scale calorimeter which has been designed for multi-purpose diagnosis and control of batch chemical processes such as polymerizations, chemical reactions or crystallizations. Because heat and mass evaporative flows are taken into account, this let-up can be regarded as a particular extension of the "usual" calorimetric reactors. As an example, this contribution deals with the particular case of evaporative crystallizations which have been reported to exhibit many control difficulties [12, 13]. Experimental runs are described. It is shown that relevant information can be obtained, for example the early detection of primary nucleation for unseeded crystallizations.

THE BENCH-SCALE CRYSTALLIZATION PLANT

Through collaborative links with the Rhône Poulenc company, the plant was designed according to the following specific industrial requirements. To provide a similarity to industrial crystallizers, an almost perfect adiabaticity of the boiling suspension has to be ensured; however, the choice of measurement devices must be realistic. For example, the accuracy of the temperature sensors involved in the on-line heat transfer calculations has to comply with the performances of industrial sensors. The software and hardware tools used should be suitable with respect to the available industrial process automation systems. For example, a standard multi-tasking operating environment for data acquisition and logging, PID control, and display functions, is required.

According to Regenass [5] and to Karlsen and Villadsen [14, 15], rather than absolute accuracy of heat measurements, advanced data treatments should be efficient in extending the industrial applicability of process-oriented studies.

A schematic representation of the microcomputer-controlled bench-scale evaporative calorimeter which was used for the experimental evaluation of advanced control policies is displayed in Fig. 1. The reaction vessel (1) is a 5-liter jacketed (2) glass reactor. Stainless steel baffles are used in conjunction with a speed-controlled stirrer. When the plant is used as a crystallizer, a Mixel-TT type impeller (4) is employed to reduce discrepancies in the particles in the slurry. The pressure of the reactor equipped with its

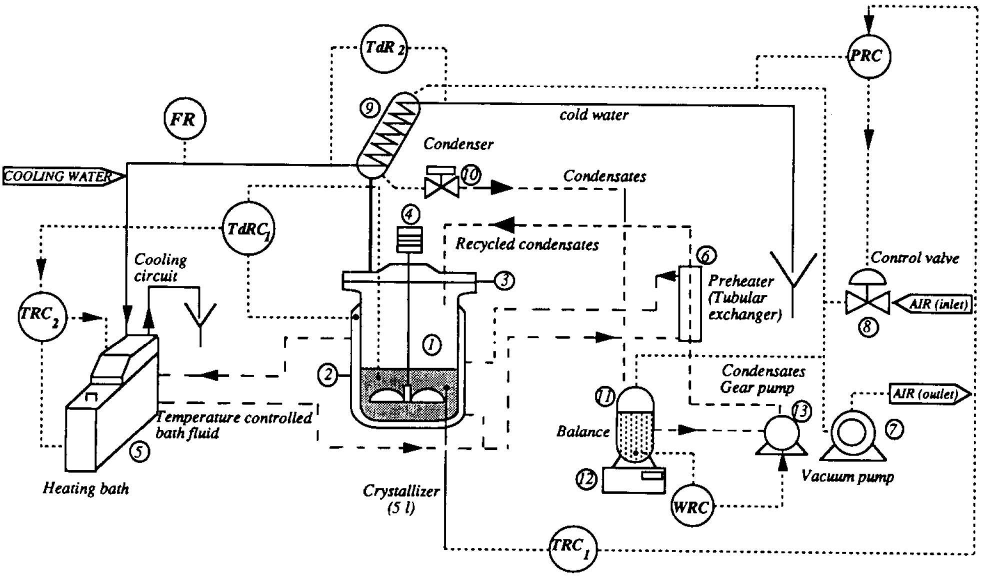

Fig. 1. Schematic representation of the microcomputer-controlled bench-scale evaporative calorimeter.

condenser (9) is controlled by means of the pneumatic control valve (8) which "feeds" the vacuum pump (7) with air.

In order to obtain similarity to industrial reactors, the thermal heat losses can be reduced through the cascade temperature-control of the jacket and of the reactor top (3). For such cases, the setpoint temperature difference between the fluid in the jacket and the reactor is set to zero, the manipulated variable being the setpoint temperature of the slave controller of the 2 kW heating bath (5).

If the valve (10) is opened, the condensates are kept in a weighted container (11). They can be recycled or not by using a small gear pump (13) and heated with the tubular exchanger (6). Cold water is used for cooling the bath and for the condensation of vapour. The temperature difference between the condenser inlet and outlet and the corresponding mass flow rate are measured.

The four primary control loops involved, i.e. TRC_2, WRC, PRC, and $TdRC_1$, are maintained by standard industrial PID controllers, the input variables being the heating power of the bath (5), the speed of the pump (13), the course of the control valve (8) and the set point temperature of the bath (5), respectively. The measured variables are the temperature of the heating bath (Pt 100), the mass of condensates (electronic balance (12)), the pressure at the top of the plant (absolute capacitance pressure transmitter) and the jacket temperature (Pt 100), respectively.

All measured, manipulated and setpoint variables are monitored by a first "PC-type" microcomputer which ensures a software multi-tasking operating

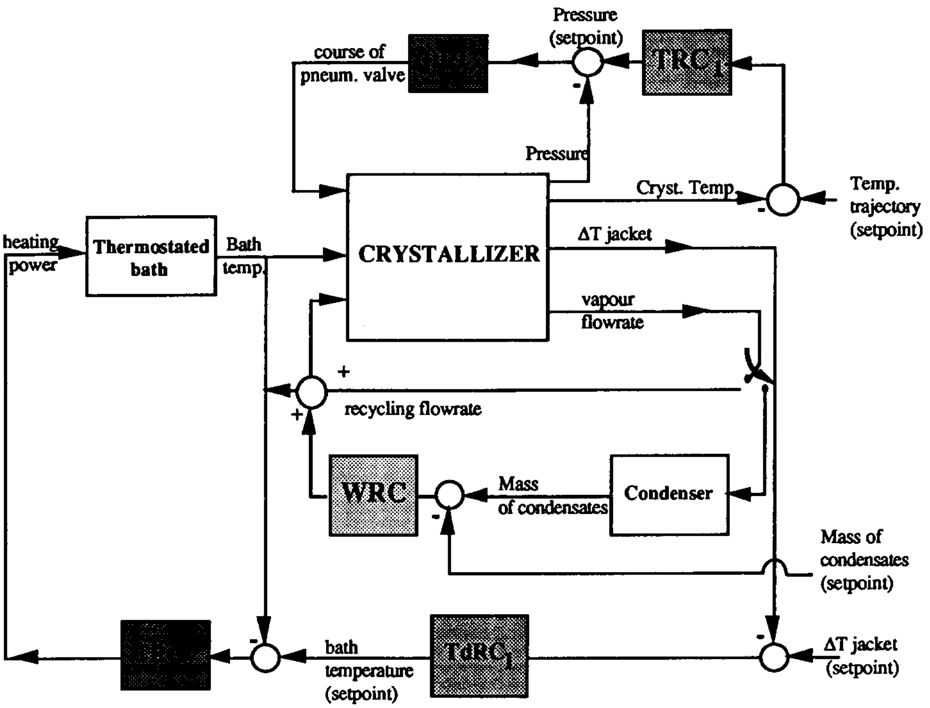

Fig. 2. Bench-scale evaporative calorimeter: block diagram of control system.

environment through the use of the GENESIS™ Control Series by ICONICS. GENESIS is a program for IBM personal computers and compatibles, providing a complete environment for creating and running industrial control schemes. GENESIS consists of two software modules: the builder module and the run-time module. The builder software itself consists of the strategy builder to create the overall strategy of control, and the display builder for graphic interface. For the development of advanced specific control and supervision tasks, a second microcomputer is linked to the previous one by means of an RS-232 C serial communication port.

The control scheme is mainly composed of five feedback control loops, as shown in Fig. 2. This structure has been designed to ensure a satisfactory flexibility of the plant for multi-purpose use, i.e. crystallization, chemical reaction, polymerization, etc. The block diagram displayed in Fig. 2 details the main measured, setpoint and manipulated variables involved.

If accurate and safe tracking of temperature trajectories is necessary, the master loop denoted TRC_1 will require advanced control policies such as adaptive algorithms [12, 13]. This loop is linked to PRC, which performs the tracking of pressure profiles through the manipulation of the course of the pneumatic valve (8). This main control block is completed by a set of 3 auxiliary controllers:

(i) $TdRC_1$ is used to impose the difference in temperature between the jacket and the slurry to be crystallized. For crystallization processes, we have chosen to ensure the adiabacity of the slurry through this device. However, any cooling or heating strategies can be implemented by setting appropriate setpoint temperature.

(ii) TRC_2 is the slave loop of the previous one. It allows any setpoint temperature profile in the jacket to be monitored.

(iii) WRC provides the user with the possibility of working with any recycling policy. For this study, we have chosen to work with total recycling of the condensates.

APPLICATION OF ON-LINE CALORIMETRY TO EVAPORATIVE CRYSTALLIZATION CONTROL

Notions of batch evaporative crystallization

Batch crystallization is an industrial chemical process which involves cooling a liquid phase, melt or solution until a crystalline solid appears. The formation of crystals, the nucleation, occurs as the temperature reaches the so-called "metastable zone" limit, and is followed by a phase of crystal growth.

For batch chemical reactors equipped with a jacket, the cooling of suspensions to be crystallized is often achieved by heat transfer through the crystallizer wall. A major problem is likely to arise in this case if a parasitic crystallization occurs on the cold wall. This phenomenon, called scaling, limits the exchange possibilities and thus, the productivity of the crystallizer. In the worst industrial situations, excessive scaling is likely to lead to stopping the batch operation. Subsequently, the possible cooling rates have to be so drastically reduced that it becomes necessary to use other cooling policies. An elegant way to avoid this phenomenon is to cool the solvent through "adiabatic" evaporation and to recycle the condensed solvent to the crystallizer. However, the main disadvantages of evaporative procedures lie in the control problems which are related to the use of a vacuum.

An appropriate temperature trajectory is generally required to ensure a satisfactory production. Indeed, the kinetics involved in crystallization processes are related to strongly non-linear functions of the temperature. Obviously, the reproducibility of quality, the control of crystal size distribution, notably the minimization of the number of fine particles, and the control of crystal shape cannot be achieved unless a reliable solution to the temperature tracking problem is available.

To obtain a temperature trajectory, industrial batch crystallizations are often operated as follows. During the initial period, the goal is to reach rapidly the neighbourhood of the nucleation point. Then, the second period consists in tracking a slight downward setpoint slope favourable to a steady

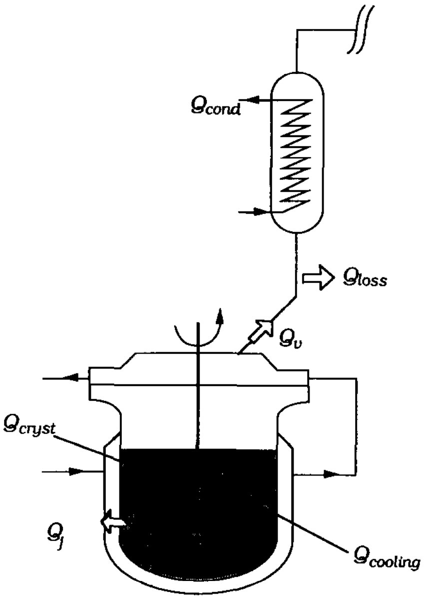

Fig. 3. Diagram of the heat balance of the bench-scale evaporative crystallizer.

crystal growth (1–5°C h^{-1}). When a sufficient crystal population is ensured, the final phase is to achieve growth but here it is possible to go faster: the temperature slope is increased up to 10–50°C h^{-1}.

Equations of thermal balance

In order to obtain real-time insight into the course of batch operations, we aimed at estimating on-line the heat power produced by crystallization. According to ref. 5, one has to bear in mind that absolute accuracy of heat measurement is less important in such process work than in research applications. As depicted in Fig. 3, the cooling rate of the boiling slurry of crystals is assumed to be related through 3 main heat terms. Namely

$$M_s C_{p_s} \frac{\mathrm{d}T}{\mathrm{d}t} = Q_j(t) - Q_v(t) - Q_{cryst}(t) = Q_{cooling}(t) \qquad (1)$$

where $Q_{cooling}(t)$ is the heat power corresponding to the temperature decay of the slurry, $Q_j(t)$ is the heat power exchanged through the jacket, $Q_{cryst}(t)$ is the heat power of crystallization (<0), and $Q_v(t)$ is the heat power removed by means of the solvent vaporization (>0).

Because both the jacket and reactor-top temperature are controlled to track the temperature of the slurry, heat losses are assumed to be negligible in eqn. (1). Given the low viscosities involved, the power consumption of the impeller is also assumed to be negligible.

A simplified estimation of $Q_j(t)$ is given by eqn. (2) which corresponds to an overall heat transfer between the fluid in the jacket and the slurry in the crystallizer

$$Q_j(t) = U_j(t)A_j\,\Delta T_j(t) = U_j(t)A_j[T_j(t) - T(t)] \tag{2}$$

During the crystallization, variations in the heat transfer coefficient U_j may be observed due to temperature decay and to changes in the physical properties of the crystallization suspension. However, it was observed that for crystallization in methanol or water, the ratio $(U_jA_j/M_sC_{p_s})$ is almost constant. Thus, the time variations of (U_jA_j) have been computed according to

$$U_jA_j(T(t)) = \delta M_sC_{p_s}(T(t)) \tag{3}$$

where δ is an empirical constant and $C_{p_s}(T)$ is given by eqn. (7).

A part of the vapour flow, corresponding to Q_v, does not reach the condenser: some heat losses upstream have been observed which cause a significant internal reflux of condensates. The corresponding heat power, denoted Q_{loss} below, is assessed by eqn. (5) which is similar to eqn. (2)

$$Q_v(t) = Q_{\mathrm{cond}}(t) + Q_{\mathrm{loss}}(t) \tag{4}$$

$$= Q_{\mathrm{cond}}(t) + (UA)_l[T(t) - T_r] \tag{5}$$

where $(UA)_l$ is an overall transfer coefficient to account for heat losses with the room at temperature T_r.

The heat term Q_{cond} is calculated from eqn. (6) assuming that the temperature increase of the cooling fluid corresponds exactly to the heat of vaporization

$$Q_{\mathrm{cond}}(t) = F_v(t)(\Delta H_v/M) = F_c(t)C_{p_c}\Delta T_c(t) \tag{6}$$

where ΔT_c is the inlet/outlet temperature increase of the cold fluid at the condenser (in K), F_c is the mass flow rate of the cold fluid at the condenser (in kg s^{-1}), F_v is the mass flow rate of vapour (in kg s^{-1}), C_{p_c} is the specific heat of the cooling fluid (in J K^{-1} kg^{-1}) and ΔH_v is the vaporization enthalpy (in J mol^{-1}).

Except for $(UA)_l$, (U_jA_j) and $(M_sC_{p_s})$, all the parameters involved in eqns. (1)–(6) are assumed constant. Indeed, these coefficients can be easily assessed via simple, off-line calculations. The terms of the product $M_sC_{p_s}$ are obviously batch dependent. The mass of slurry should be known and its specific heat is computed as a known function of the temperature

$$C_{p_s}(t, T) = f(T(t)) \tag{7}$$

A typical set of parameters involved in eqns. (1)–(5) is given below. These data correspond to the crystallization of the Rhône Poulenc weedkiller in methanol: $M_s = 3.65$ kg; $T_r = 308$ K; $C_{p_s} = f(T) = 2466[1 + 8.5 \times 10^{-4}(T - 278)]$; $\delta = 2.2 \times 10^{-3}$ SI implies e.g., $U_jA_j(323) = 20.56$ W K^{-1};

$(UA)_l = 0.35\ \mathrm{W\ K^{-1}}$. Further results of this crystallization are given in the next sections.

The identification algorithm

Let $y(t)$ be a variable to be predicted, given by eqn. (8) and rewritten in the linear regressive form in eqn. (9) which is more suitable for recursive identification

$$\begin{aligned}\hat{y}(t) &= \hat{Q}_{\mathrm{loss}}(t) + \hat{Q}_{\mathrm{cryst}}(t)\\ &= (\widehat{UA})_l(t)(T(t) - T_r) + \hat{Q}_{\mathrm{cryst}}(t) \qquad (8)\end{aligned}$$

$$\hat{y}(t) = \hat{\theta}^{\mathrm{T}}(t)\varphi(t) \qquad (9)$$

where θ and φ are two-dimensional vectors, and the exponent T denotes a transposed vector, e.g., $\varphi^{\mathrm{T}}(t) = [\varphi(t)]^{\mathrm{T}}$. So

$$\begin{cases}\theta^{\mathrm{T}}(t) = [(UA)_l(t) & + Q_{\mathrm{cryst}}(t)]\\ \varphi^{\mathrm{T}}(t) = [T(t) - T_r & 1]\end{cases}$$

The parameter $y(t)$ is considered as the actual process output. Thus, it is assumed that the unknown part of the thermal balance depends on only two θ parameters. Thus, the key-term $Q_{\mathrm{cryst}}(t)$ is considered as a time-varying parameter. The overall coefficient $(UA)_l$ provides the possibility of taking into account modelling uncertainties in terms of heat losses. So, according to the main thermal balance, eqn. (1), and to eqns. (2)–(5), $y(t)$ is simply calculated from directly available measurements, i.e.

$$y(t) = Q_j(t) - Q_{\mathrm{cond}}(t) - M_s C_{p_s}\, \mathrm{d}T/\mathrm{d}t \qquad (10)$$

An average cooling slope $\mathrm{d}T/\mathrm{d}t$ is computed from sliding windows of data $[T(t-\mathrm{j})$ to $T(t)]$. So, the recursive identification policy which was applied is now straightforward. Let $\varepsilon(t)$ be a so-called prediction error calculated from eqns. (8)–(10), i.e.

$$\varepsilon(t) = \hat{y}(t) - y(t) \qquad (11)$$

Then, the goal is to obtain on-line an estimate for θ that minimizes $\varepsilon(t)$. Such an estimate is obtained by using a recursive least-squares algorithm (RLS), which is assumed to fit an optimal equilibrium of the balance.

For non-stationary systems such as cooling by using a vacuum, basic RLS schemes are known to show a lack of ability to track time-varying parameters. In order to ensure that the algorithm retains its viability, several variants have been described in the literature [16]. In particular, forgetting factors have been introduced to discount old information in favour of new process data. Therefore, we have applied an identification procedure with two forgetting factors developed by Landau [17], which was designed to ensure global asymptotic stability of the parameter estimator.

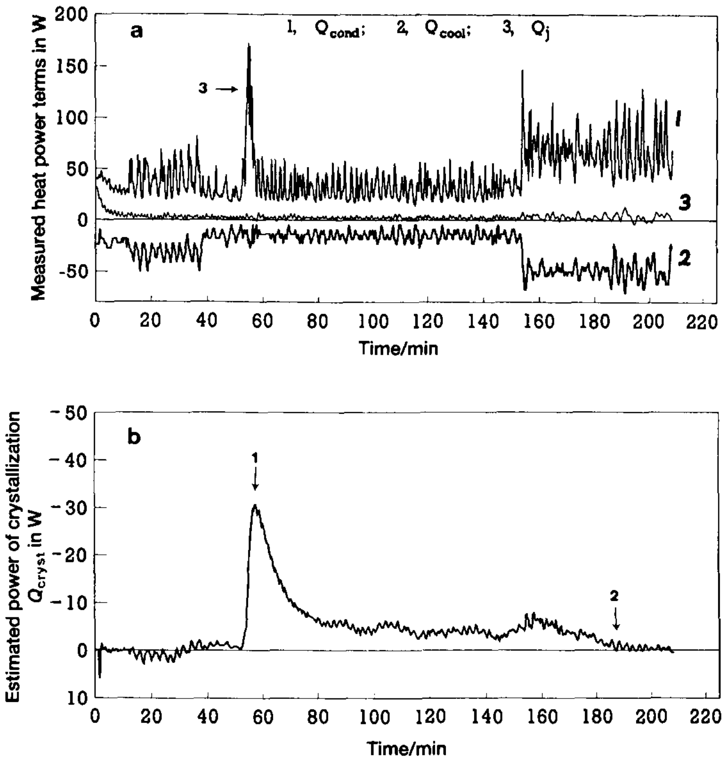

Fig. 4. On-line estimation of the power $Q_{\mathrm{cryst}}(t)$ during a batch evaporative crystallization: a, data; and b, estimate.

Thus, the minimization of the prediction error (11) is obtained by using the following recursive least-squares algorithm with two forgetting factors, denoted λ_1 and λ_2

$$\hat{\theta}(t+1) = \hat{\theta}(t) + F(t)\varphi(t)\varepsilon(t+1) \tag{12a}$$

$$F(t+1) = \frac{1}{\lambda_1(t)}\left[F(t) - \frac{F(t)\varphi(t)\varphi^{\mathrm{T}}(t)F(t)}{\dfrac{\lambda_1(t)}{\lambda_2(t)} + \varphi^{\mathrm{T}}(t)F(t)\varphi(t)}\right] \tag{12b}$$

$$\varepsilon(t+1) = \frac{y(t+1) - \hat{\theta}^{\mathrm{T}}(t)\varphi(t)}{\dfrac{\lambda_1(t)}{\lambda_2(t)} + \varphi^{\mathrm{T}}(t)F(t)\varphi(t)} \tag{12c}$$

where

$$0 < \lambda_1(t) \leqslant 1 \quad \text{and} \quad 0 \leqslant \lambda_2(t) < 2 \tag{12d}$$

EXPERIMENTAL RESULTS

Figure 4 shows typical data and estimates obtained during batch evaporative crystallization of a given weedkiller in methanol. With a sampling time of 10 seconds, $y(t)$ is given by eqn. (8); three heat terms of the balance are displayed in Fig. 4a. In this case, one can easily see that the heat exchanged through the jacket Q_j has been small (curve 3).

Due to the oscillatory behaviour of the vapour flows and to the limitations of the temperature decrease measurements, the calculated flows $Q_{cond}(t)$ (see curve 1 in Fig. 4a) and $Q_{cooling}(t)$ (see curve 2 in Fig. 4a) appear to be very noisy. However, as one can see in Fig. 4b, the estimated heat of crystallization is realistic, more accurate and smoother than the measured heat data involved. Before nucleation, which looks like an impulse response (arrow 1 in Fig. 4b), the heat of crystallization, as expected, is satisfactorily found to be almost zero. After nucleation, some estimation of the crystal growth is provided by the RLS. At the end of the batch, one can verify that no significant crystallization occurs because no heat is detected (arrow 2 in Fig. 4b).

As outlined in the introduction, several major applications based upon the "soft sensoring" of the heat of crystallization are possible. It was reported that using the heat terms, notably $Q_v(t)$, allows adaptive supervision of the temperature-tracking system [18].

Moreover, the estimation results allow an extension of diagnostic and control possibilities for batch operations. For example, correlations between key parameters of the particles, e.g. mean crystal size, and the amounts of fine particles present, and the shape of the nucleation peak could be assessed in further studies [19].

Such relationships should provide industrialists with a means of cutting particle analysis costs. Moreover, according to these correlations, it might be possible to design and evaluate new strategies for batch crystallizations.

CONCLUSIONS

A process-oriented bench-scale evaporative calorimeter has been designed and tested with aim of developing industrial hardware and software tools. In particular, if the general trend in chemical process calorimetry has been to increase the accuracy of the apparatus, but still keeping data treatment simple [14, 15], our purpose has been to compensate noisy and, thus, insufficiently accurate data by recursive identification algorithms.

The case of batch unseeded evaporative crystallizations has been reported as an example. Using an RLS identification algorithm, some satisfactory on-line estimates of the heat of crystallization have been obtained which have led to a better real-time understanding of the process and to new possibilities for advanced control and monitoring policies.

REFERENCES

1 H. Schuler and C.U. Schmidt, Calorimetric state estimators for chemical reactor diagnosis and control: review of methods and applications, Chem. Eng. Sci., 47(4) (1992) 899–915.

2 H.U. Moritz, Polymerization calorimetry—a powerful tool for reactor control, in K.H. Reichert and U. Geiseler (Eds.), Polymer Reaction Engineering, VCH Verlag, Berlin, 1989, pp. 248–266.
3 C.U. Schmidt and K.H. Reichert, Reaction calorimeter. A contribution to safe operation of exothermic polymerization, 10th ISCRE Chem. Eng. Sci., 43 (1987) 2133–2137.
4 B. Grob, R. Riesen and K. Vogel, Reaction calorimetry for the development of chemical reactors, Thermochim. Acta, 114 (1987) 83–93.
5 W. Regenass, Calorimetric monitoring of industrial chemical processes, Thermochim. Acta, 95 (1985) 351–368.
6 P. De Valliere and D. Bonvin, Experimental estimation of concentrations from reactor temperature measurement, IFAC Symp. AdChem'88, Lyngby, IFAC Proc. Ser., Pergamon, Oxford, 1988.
7 I.W. Marison and U. von Stockar, A novel bench-scale calorimeter for biological process development work, Thermochim. Acta, 85 (1985) 493–496.
8 I.W. Marison, B. Birou and U. von Stockar, Use of a novel heat-flux calorimeter for the measurement of heat generated during growth of *K. fragilis* on lactose, Thermochim. Acta, 85 (1985) 497–500.
9 L. Hub, Universal system for investigation of thermic hazards, Thermochim. Acta, 85 (1985) 361–364.
10 J.R. Bourne, M. Buerli and W. Regenass, Heat transfer and power measurements in stirred tanks using heat flow calorimetry, Chem. Eng. Sci., 36 (1981) 347–354.
11 A.J. Eckles and P.H. Benz, The basics of vacuum processing, Chem. Eng., 99(1) (1992) 78–86.
12 G. Févotte and J.P. Klein, Non linear control of batch evaporative crystallizers, in K. Najim and J.P. Babary (Eds.), Prepr. IFAC Symposium AdChem'91, Toulouse, France, 1991.
13 G. Févotte and J.P. Klein, Robust adaptive temperature tracking for industrial batch evaporative crystallizers, in I.D. Landau et al. (Eds.), Prepr. IFAC Symposium ACASP'92, Grenoble, France, 1992.
14 L.G. Karlsen and J. Villadsen, Isothermal reaction calorimeters — I. A literature review, Chem. Eng. Sci., 42(5) (1987) 1165–1173.
15 L.G. Karlsen and J. Villadsen, Isothermal reaction calorimeters — II. Data treatment, Chem. Eng. Sci., 42(5) (1987) 1153–1164.
16 S.L. Shah and W.R. Cluett, Recursive least squares based estimation schemes for self tuning control, Can. J. Chem. Eng., 69 (1991) 89–96.
17 I.D. Landau, Adaptive Control — The Model Reference Approach, Marcel Dekker, New York, 1979.
18 G. Févotte and J.P. Klein, Application of on-line calorimetry to the advanced control of batch crystallizers, Chem. Eng. Sci., in press.
19 G. Févotte and J.P. Klein, Identification en-ligne du bilan thermique de cristallisoirs discontinus, 4ème Congrès Français de Génie des Procédés, 29 July 1993, Grenoble, France, pp. 63–68, ed. GFGP/Lavoisier, Paris, France (in French).