

## The Use of On-line Calorimetry in the Optimisation of Isothermal Semi-Batch Reactors.

O. Ubrich<sup>+</sup>, B. Srinivasan\*, P. Lerena<sup>°</sup>, D. Bonvin\*, F. Stoessel<sup>+</sup>

<sup>+</sup> Institut de Génie Chimique, Ecole Polytechnique Fédérale de Lausanne

\* Institut d'Automatique, Ecole Polytechnique Fédérale de Lausanne

CH-1015 Lausanne, Switzerland

<sup>°</sup>Swiss Institute for the Promotion of Safety & Security

CH-4002 Basel, Switzerland

### Abstract

This paper considers the maximisation of conversion by manipulating the input flowrate for an exothermic second-order esterification reaction (propionic anhydride + 2-butanol) performed in a semi-batch reactor. Safety considerations impose bounds on the heat release rate in normal operation and on the maximum attainable temperature in the case of cooling failure. The optimal input flowrate is calculated on-line using a heat balance over the reactor.

### Keywords

Process Control, Safety, Optimisation, Isothermal, Calorimetry, Semi-batch reactors.

### 1. Introduction

One operational objective of the chemical industries is to increase the production or selectivity using safe processes. Since the reactions are often exothermic, they may present a risk in case of loss of control of the reactor. In order to enhance the control of the reaction, batch operation is often turned into semi-batch operation allowing to control the reaction rate via the feed rate of one of the reactants (Abel and Marquardt 1998).

The control and optimisation of semi-batch reactors have been discussed extensively in the literature. On the one hand, in the last decades, open-loop optimisation based on mathematical models has been proposed (Lim et al. 1986, Arzamendi et al. 1989, Marchal-Brassely et al. 1989). It appears that significant improvement can be obtained with well-chosen input flowrates. On the other hand, predictive runaway regions using selected kinetic models have been developed (Strozzi and Zaldívar 1994, Wu et al. 1998). It appears that accidents can be foreseen and so avoided. Also, some research tries to couple the safety and optimisation aspects (Regenass 1997). The problem of the control of accumulation of non-converted reactants by modulating the feed was first addressed by Gyax (Iscre 10<sup>th</sup>), ESCIS heft 8. The optimization of the productivity under safety constraints in semi-batch reactors, taking this problem of accumulation into account was extensively studied by different authors: (Toulouse et al, 1996), and more recently by (Abel et al. 2000) and (Abel and Marquardt 2000). For these methods, kinetics models have to be available.

However, for the fine chemical industry, models are very rarely available (Heinzle and Hungerbühler 1997). Thus, on-line measurements are used

successfully utilized in polymer control and optimisation (Urretabizkaia et al. 1994). But this method only provides measurements approximately every 10 minutes. Spectroscopic methods can also be used (Rein et al. 1995). However, it possesses three main drawbacks. Firstly, most investigations are based on the Beer-Lambert law, which is valid only for low concentrations. In contrast, the concentrations are often high in production reactors. Secondly, for non isothermal processes, the influence of temperature variations has to be considered. The relationship between absorbance and temperature is complex (Wulfert et al. 1998). Finally, safety considerations are difficult to take into account. Indeed, safety considerations are often related to heat accumulation. It is possible to evaluate the heat production using spectroscopic data only if a kinetic model and thermal data are available.

Reaction calorimetry represents an alternative experimental technique (Sáenz de Buruaga et al. 1997). The use of calorimetry for on-line optimisation under safety constraints presents some advantages. This method is based on easily available signals such as temperatures, flows and pressures (Schuler and Schmidt 1992). It allows a control of the reactor based on the heat release (Regenass 1985, Schimetzek and Giesbrecht 1998). Moreover, its results can be directly used for scale-up.

In this article, it is shown that calorimetry can be used to optimise a process on-line under safety constraints without the use of a detailed model and complex mathematical tools.

The paper is organised as follow. Section 2 formulates the problem, while Section 3 deals with calorimetric measurements. In Section 4,

experimental results are proposed in Section 5. Finally, Section 6 concludes the paper.

## 2. Problem formulation

### 2.1 Chemical reaction

The esterification of propionic anhydride with 2-butanol is considered:

The reaction, which is symbolised by



is known to be a second-order reaction, i.e. first order in each reactant. This reaction is taken as a test reaction because its kinetic parameters are known (Galván et al. 1996), but these will only be used for verifying the experimental optimisation results.

### 2.2 Safety considerations

Before scaling-up an isothermal process, and according to safety considerations, two important questions have to be answered:

- Is the system capable of remaining isothermal in normal operation? In other words, can the heat released by the reaction be removed under normal operation?
- Can the system be prevented from running away in the case of a cooling failure?

Under normal operating conditions, in order to remain isothermal, the system has to produce less heat than can be removed by the cooling system of the reactor:

$$q_{rx}(t) < q_{ex,max}(t) \quad (2)$$

where  $q_{rx}$  is the rate of heat production by the chemical reaction and  $q_{ex,max}$  the available heat exchange rate.

In the case of a cooling failure, the maximum attainable temperature has to remain inferior to a critical value. Runaways for exothermic reactions are often described by the scenario represented in Figure 1. Following a cooling failure, the system can be considered adiabatic. Therefore, the heat produced by the chemical reaction can no longer be removed by the cooling system. This is especially true for industrial reactors where heat losses can be neglected. Even if the feed is immediately stopped, if non reacted material is still present in the reactor, the chemical reaction continues. The heat produced results in temperature increase up to  $T_{cf}$  (temperature in the case of cooling failure). The  $T_{cf}$ -value depends upon the process temperature, the amount of non-converted reactants and the total adiabatic temperature increase (Hugo et al. 1988):

$$T_{cf}(t) = T(t) + \min(N_A(t), N_B(t)) \frac{(-\Delta H_r)}{\rho C_p V(t)} \quad (3)$$

The term  $\min(N_A, N_B)$  serves to calculate the

following the failure, and  $(-\Delta H_r)/\rho C_p V$  represents the adiabatic temperature increase.

For safety considerations, the worst case scenario is considered. Therefore, the concept of MTSR (Maximum Temperature Synthesis Reaction) developed by Gyax (1988), is introduced:

$$MTSR = \max_t T_{cf}(t) \quad (4)$$

This concept is used nowadays by several companies (Nomen et al. 1995, Elvers et al. 1995). The MTSR-value is used to predict whether the boiling point of the system can be reached or if the reaction medium can trigger some exothermic decomposition reactions (Lerena et al. 1996). In this case, a cooling failure can lead to an accident with severe consequences.

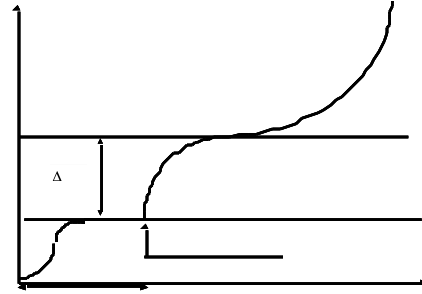


Fig. 1 The runaway scenario (Gyax, 1988)

### 2.3 Dynamic model

The reaction system can be modeled as follows:

$$\begin{aligned} N_A &= -rV & N_A(0) &= N_{A,0} \\ N_B &= c_{B,in}u - rV & N_B(0) &= N_{B,0} \\ V &= u & V(0) &= V_0 \end{aligned} \quad (5)$$

where  $r$  is the reaction rate,  $c_{B,in}$  represents the concentration of B fed to the reactor,  $N_{A,0}$  and  $N_{B,0}$  are the initial mole numbers of A and B, respectively, and  $V_0$  the initial volume in the reactor.

From System (5), the following expressions can be obtained for  $N_A$  and  $N_B$ :

$$N_A = N_{A,0}(1 - x_A) \quad (6)$$

$$N_B = N_{B,0} + c_{B,in}(V - V_0) - N_{A,0}x_A \quad (7)$$

where  $x_A$  is the molar conversion of A.

Since a simple reaction is considered, the molar conversion equals the thermal conversion. The

thermal conversion can be evaluated on-line from the heat power generated by the chemical reaction:

$$x_{th}(t) = \frac{\int_0^t q_{rx}(t') dt'}{\min(N_{A,0}, N_{B,0})(-\Delta H_r)} \quad (8)$$

where  $-\Delta H_r$  is the heat of reaction and  $q_{rx}$  the heat rate produced by the chemical reaction.

In this work,  $q_{rx}$  will be estimated via calorimetric measurements, without knowledge of kinetic parameters. Thus, Equations (3)-(8) enable calculation of  $T_{cf}$ . The safety constraint simply states:

$$T_{cf}(t) \leq T_{max} \quad (9)$$

where  $T_{max}$  is the upper bound on the temperature.

#### 2.4 Optimisation problem

The optimal control problem consists, for a given final time, of adjusting the feed rate  $u(t)$  to maximise the production of the ester D whilst meeting specific operational and safety constraints.

The constraints of this optimisation problem are:

- The physical limitation of the volume:

$$V(t) \leq V_{max} \quad (10)$$

- The physical bounds on the feed rate:

$$u_{min} \leq u(t) \leq u_{max} \quad (11)$$

- The safety constraints:

$$q_{rx}(t) \leq q_{ex,max}(t) \quad (12)$$

$$T_{cf}(t) \leq T_{max} \quad (13)$$

Visser et al. (2000) have shown that, in the terminal-cost optimization of control-affine systems, the solution either lies on path constraints (input bounds or state constraints) or is singular. Ubrich et al. (1999a) showed for an isothermal reaction system involving safety constraints that the solution has at most five distinct arcs characterized by path constraints (see their Fig. 9). With the reaction system at hand, it is not possible to reach the operational safety constraint (12). Furthermore, the initial conditions  $N_{A,0}$  and  $N_{B,0}$  were so chosen that the system is initially on the safety constraint (13). Thus, the first two arcs in Ubrich et al. (1999a) do not exist here, and conversion will be maximized for  $T_{cf} = T_{max}$ . Furthermore, as soon as  $N_A(t) < N_B(t)$ ,  $T_{cf}$  will no longer depend on  $N_B$ , i.e., on the input  $u$ . Thus, if there is still material B to be fed,  $u(t)$  can be switched to  $u_{max}$  until  $V(t)$  reaches  $V_{max}$ , at which point  $u = u_{min}$ . If the total number of moles of B that can be added is less than the number of moles of A,  $u(t)$  will switch to  $u_{min} = 0$  as soon as all the B has been added.

This approach to dynamic optimization is always applicable to control-affine terminal-cost problems. Of course, only one constraint per available input can be active at any point in time, namely the most restrictive one. However, the number of constraints that can be active during the duration of the batch is not limited (see e.g. the 5 constraints that are followed in Ubrich et al.'s example).

### 3. Calorimetric measurements

On-line calorimetric measurements will be used to estimate  $q_{rx}(t)$  and evaluate  $x_{th}$  according to Eq. (8).

Reaction calorimetry is based on an energy balance over the reactor (see Fig. 2):

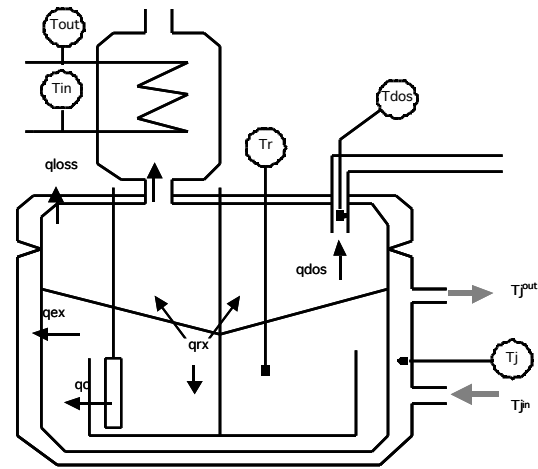


Fig. 2 Heat balance over the reactor.

$$m^{(i)} c_p^{(i)} \frac{dT_r}{dt} = \underbrace{q_{rx} + q_{in} + q_{mix} + q_c + q_{st}}_{inflow} - \underbrace{q_{ex} + q_{loss}}_{outflow} \quad (14)$$

where  $m^{(i)}$  and  $c_p^{(i)}$  are the mass and the heat capacity of the  $i^{th}$  component in the reaction mixture,  $q_{in}$ ,  $q_{mix}$  and  $q_{loss}$  are the power terms corresponding to: (i) feeding at a temperature different from  $T_r$ , (ii) a possible mixing enthalpy, and (iii) the heat lost to the surroundings.  $q_c$  and  $q_{st}$  are the heating power resulting from the calibration and the stirrer, respectively. The terms  $q_{rx}$ ,  $q_{in}$ ,  $q_{mix}$ ,  $q_c$  and  $q_{st}$  represent inflow terms, while  $q_{ex}$  and  $q_{loss}$  are the outflow terms.

Thus, in theory,  $q_{rx}$  can be calculated from Eq. (14) if the other terms can be evaluated or measured with sufficient accuracy. The various terms in Eq (14) are described below.

#### 3.1 Accumulation of heat

The reaction is performed isothermally. Therefore, the heat accumulation is negligible.

$$\sum_i m^{(i)} c_p^{(i)} \frac{dT_r}{dt} = 0 \quad (15)$$

### 3.2 Heat effect of the feed stream

The heating effect due to the difference in temperature between the feed temperature  $T_{in}$  and the reactor medium temperature  $T_r$  is given by:

$$q_{in} = u \rho_{in} c_{pin} (T_{in} - T_r) \quad (16)$$

where  $\rho_{in}$  and  $c_{pin}$  are the density and the heat capacity of the feed stream.

### 3.3 Enthalpy of mixing

It appears sometimes that when two reactants at the same temperature are mixed, a significant drop in temperature of the reaction mass occurs. This is due to the endothermic heat of mixing. In the considered reaction, the time constant of mixing is assumed to be negligibly small compared to the reaction time constant. Thus, the heat effect due to mixing is modeled as a static term:

$$q_{mix} = \frac{(-\Delta H_{mix})u}{V_{mol}} \quad (17)$$

where  $\Delta H_{mix}$  is the mixing enthalpy, and  $V_{mol}$  the molar volume of the added 2-butanol.

### 3.4 Calibration power

Calibrations are performed *before* the experiment. Therefore, during the reaction,  $q_c$  is zero.

$$q_c = 0 \quad (18)$$

### 3.5 Stirrer power

The stirrer power is neglected here.

$$q_{st} = 0 \quad (19)$$

### 3.6 Heat exchange

Assuming steady-state conditions,  $q_{ex}$  can be calculated from a heat balance on the jacket:

$$q_{ex} = F^{cool} c_p^{cool} (T_j^{out} - T_j^{in}) \quad (20)$$

where  $F^{cool}$  and  $c_p^{cool}$  are the mass flowrate and the heat capacity of the cooling medium,  $T_j^{out}$  and  $T_j^{in}$  the outlet and inlet temperatures of the cooling medium, respectively.

If the flow rate of the cooling medium is high, the temperature variation in the jacket is negligible and  $T_j^{out} \approx T_j^{in}$ . This is often the case in reaction calorimeters. In this case, the heat exchanged through the reactor wall can be expressed as:

$$q_{ex} = U A (T_r - T_j) \quad (21)$$

In industrial production, Eq. (20) is used preferably to Eq. (21), because  $U$  can vary and is difficult to evaluate on-line. Some methods using a "Temperature oscillation mode" in the jacket exist now (Carloff et al. 1994, Bou Diab 1999) but are not often used yet. Therefore, Eq. (20) is normally more accurate and useful than Eq. (21). However, the calorimeter used here to carry out the experiment is the RC1 proposed by Mettler Toledo. This very reliable machine uses Eq (21) to calculate the heat flowrate.

### 3.7 Heat losses

The heat losses depend not only on the temperature difference between the reaction mass and the boiling point, but also on the material and the geometry of the reactor. Because of its geometrical dependence, this term is less important for industrial than for laboratory reactors. This is another strong reason for using on-line calorimetry in industrial production.

In order to perform reaction calorimetry on-line, the base line needs to be known, i.e. what the measurement would be without heat released by the chemical reaction. With the experimental setup used in this work, i.e. constant surrounding temperature and non heated reactor cover, the heat losses are mainly due to some evaporation of the reaction medium. Some vapor may condensate at the colder cover and some colder condensate droplets flow back to the reactor. This can be considered to be the major contribution to heat losses. Therefore it can be assumed that the heat losses are proportional to the overall vapor pressure of the system:

$$q_{loss} = \alpha \sum_j x_j P_j \quad (22)$$

where  $\alpha$  is a constant,  $x_j$  and  $P_j$  are the molar fraction and the vapour pressure of component  $j$ , respectively.

The vapour pressure can be estimated using Clausius–Clapeyron equation:

$$P(T_1) = P(T_2) \exp \left( \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right) \quad (23)$$

where  $\Delta H_v$  is the heat of vaporisation,  $R$  the molar gas constant,  $P(T_1)$  and  $P(T_2)$ , the vapour pressure at temperature  $T_1$  and  $T_2$ , respectively.

The factor of proportionality  $\alpha$  in Eq. (22) is evaluated by trial and error adjustments of the baseline using on-line experiments.

### 3.8 Integrated heat balance

Integration of Eq. (14) for isothermal conditions gives:

$$Q_{rx}(t) = Q_{ex}(t) + Q_{loss}(t) - Q_m(t) - Q_{mix}(t) \quad (24)$$

Where  $Q_i(t)$  is the energy term that corresponds to the integral of the power term  $q_i(t)$ :

$$Q_i(t) = \int_0^t q_i(t') dt' \quad (25)$$

## 4. Experimental implementation

### 4.1 Experimental setup

With the commercially available software of the calorimeter, it is not possible to calculate the optimal feed rate on-line. Thus, an external computer is used, which performs the on-line heat balance calculations and controls the addition of reactant. It is connected to a balance that can read the increment reactor mass  $m$  and to a ProMinent gamma G/4b pump (see Figure 3). This is a membrane pump which gives a stroke each time a pulse is applied.

The calorimeter is used to control the reactor temperature which is maintained constant.

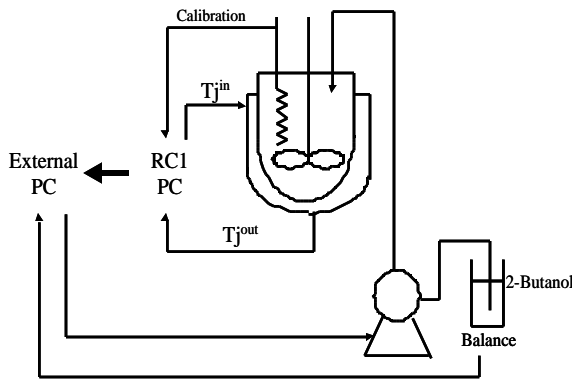


Fig. 3 Calorimeter linked to an external computer.

### 4.2 Choice of sampling time

The mixing of 2-butanol with the reaction medium is accompanied by a temperature decrease due to the temperature difference between the feed and the reactor medium but also to the negative enthalpy of mixing.

The effect of adding 2-butanol to the reactor is depicted in Figure 4. The temperature difference ( $T_r - T_j$ ) is represented for a sampling time of 8 seconds, which is large enough to allow the balance to stabilize after a feeding pulse but small enough to allow an adequate representation of the temperature variations. The large and the small integrated areas correspond to  $Q_{ex}$  and  $(Q_{in} + Q_{mix})$  for a sampling period, respectively.

### 4.3 Optimisation algorithm

Since the optimization objective is to be on the safety constraint  $T_{cf}(t) = T_{max}$  whenever possible, the following control law is introduced:

$$u(t) = \begin{cases} 0 & \text{for } T_{cf}(t) > T_{max} - \Delta T_s \\ u_{max} & \text{for } T_{cf}(t) < T_{max} - \Delta T_s \end{cases} \quad (26)$$

where  $\Delta T_s$  is an imposed safety factor or back off (Visser 1999).

The data processing and optimisation algorithm is depicted in Figure 5. It is programmed within LabView .

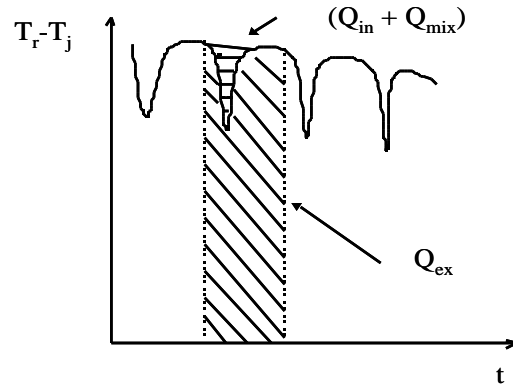


Fig. 4 Evolution of  $T_r - T_j$  vs. time for a semi-batch process.

The integration of the signals is performed using the rectangular approximation, which is justified by the small sampling time. For example, at the discrete time  $t_k$ ,  $Q_i(k)$  can be expressed as:

$$Q_i(k) = Q_i(k-1) + \int_{t_{k-1}}^{t_k} q_i(t) dt = Q_i(k-1) + \Delta Q_i(k) \quad (27)$$

Thus, the discrete expression for  $Q_{rx}(k)$  follows from Eq. (24) and reads:

$$Q_{rx}(k) = Q_{rx}(k-1) + \Delta Q_{ex}(k) + \Delta Q_{loss}(k) - \Delta Q_{in}(k) - \Delta Q_{mix}(k) \quad (28)$$

## 5. Experimental results

### 5.1 Calibration

#### 5.1.1 Evaluation of the heat of reaction

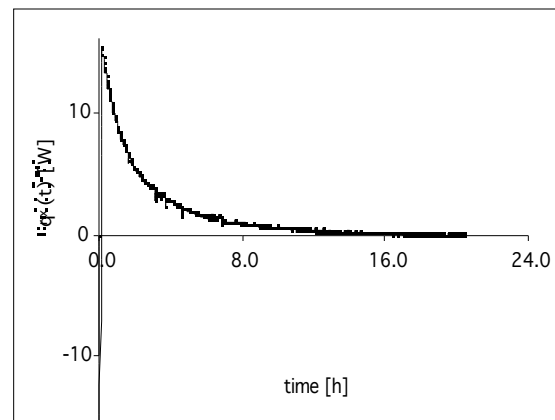


Fig. 6 Evolution of the power released by the reaction for an isothermal batch run at 70 °C.

In order to perform the on-line optimisation, the heat of reaction has to be known very accurately. For its evaluation, an isothermal (70 °C) batch run is performed in the calorimeter in which 2.5 moles

of A are added to 2.5 moles of B. Integration of the reaction power gives (Figure 6):

$$Q = 52.5 \text{ kJ/mol} \quad (29)$$

However, this value does not represent the correct heat of reaction. Indeed, on the one hand, when 2-butanol previously heated at the reaction temperature is added to propionic anhydride, there is a significant drop in temperature. This is due to the negative mixing enthalpy. On the other hand, the reaction is very slow and therefore not totally finished after 20 hours. With the help of spectroscopic measurements, it can be determined that the final conversion is 90%. For these two reasons, the value given by the calorimeter has to be corrected (Regenass 1997).

In order to evaluate the mixing enthalpy, mixing of the two products is performed at 25 °C in a very sensitive calorimeter (Calvet calorimeter Setaram C80, 1996). At this temperature, the chemical reaction can be considered negligible (Ubrich et al. 1999b). The result of this experiment is depicted in Figure 7 and gives:

$$\Delta H_{mix} = -4.2 \text{ kJ/mol} \quad (30)$$

Therefore, the 'corrected' value of the heat of reaction is:

$$\Delta H_r = -52.5/0.9 - 4.2 = -62.5 \pm 1 \text{ kJ/mol} \quad (31)$$

Strozzi et al. (1997) proposed  $-62.99 \text{ kJ/mol}$  for this reaction.

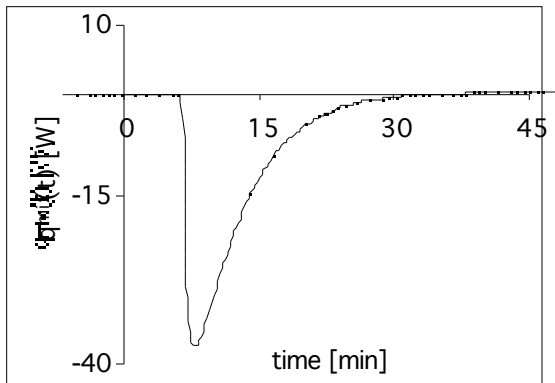


Fig.7 Determination of the mixing enthalpy of propionic anhydride and 2-butano at 25 °C as given by the C80-Calorimeter.

### 5.1.2 Evaluation of thermal quantities

In order to implement the optimisation strategy, it is necessary to know the heat capacity ( $c_p$ ), the overall heat transfer coefficient ( $U$ ) and the density ( $\rho$ ) of the reaction mass during the experiment.

The heat capacity was measured in the calorimeter for the initial and final reaction masses. The values are approximately the same. Therefore, it is postulated that the heat capacity does not change during the experiment and, thus, it is considered constant.

Similarly, the overall heat transfer coefficient is evaluated from calibration performed with the calorimeter for the initial and for the final reaction mass too. The values are approximately the same.  $U$  is therefore considered constant during the reaction.

Finally, the densities of the four different products are close to each other. The average value is taken as the constant density of the reaction medium.

### 5.2 On-line results

The reactor is initially filled with  $N_{A,0}$  moles of propionic anhydride and heated to the desired temperature of 70 °C for isothermal operation. In order to already be on the safety constraint at time  $t=0$ , ie.  $T_{cf}(0) = T_{max} - \Delta T_s$ ,  $N_{B,0}$  moles of 2-butanol preheated at 70 °C are also added to the reactor.  $N_{B,0}$ :

$$N_{B,0} = (T_{max} - \Delta T_s - T_r(0)) \frac{\rho c_p V(0)}{(-\Delta H_r)} \quad (32)$$

Then the remaining B is added through the inlet feed according to the optimisation procedure.

Figure 8 shows the evolution of  $T_{cf}$  calculated on-line in relation to  $T_{max}$ . As predicted, the system rides on the constraint until it cannot reach it anymore.

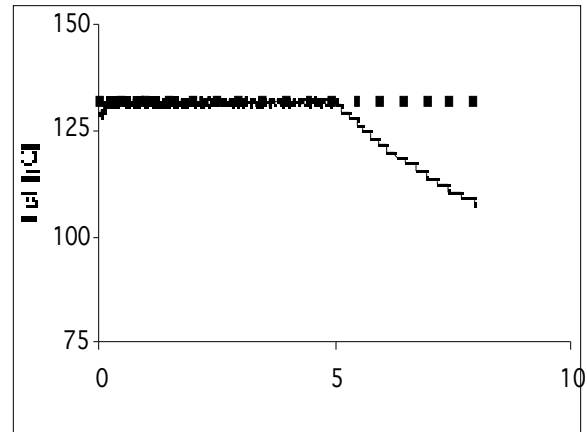


Fig. 8 Evolution of  $T_{cf}$  evaluated on-line (solid line) in relation to  $T_{max}$  (dash line).

Figure 9 represents a comparison between:

- (i) the on-line estimated chemical conversion.
- (ii) the conversion estimated upon completion of the reaction from the calorimeter data.
- (iii) the chemical conversion obtained by simulation using the kinetic parameters of the reaction.

Initialisation

$V(0)=V_0$   
 $x_{th}(0)=0$   
 $Q_{rx}(0)=0$   
 $m(0)=0$   
 $k=0$

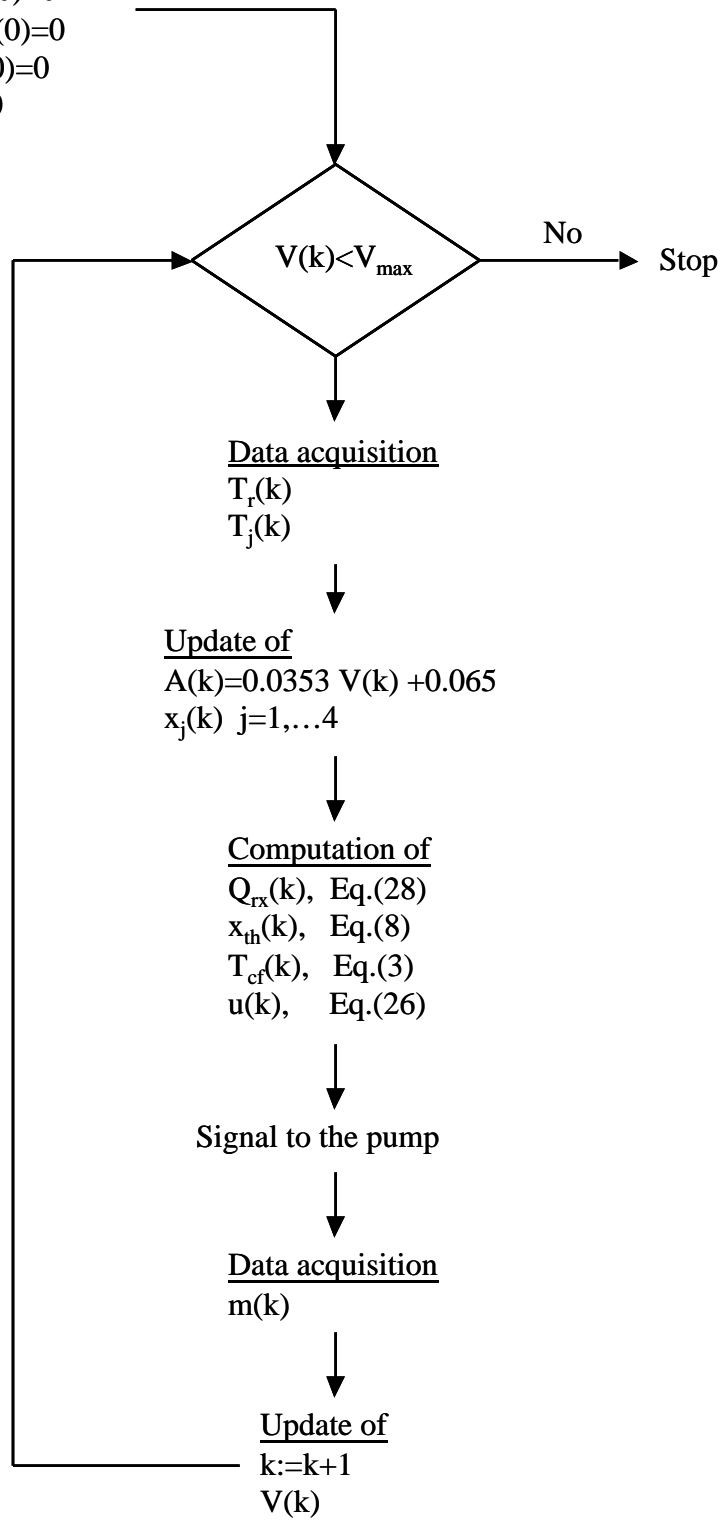


Fig. 5 LabView program for implementing the optimisation

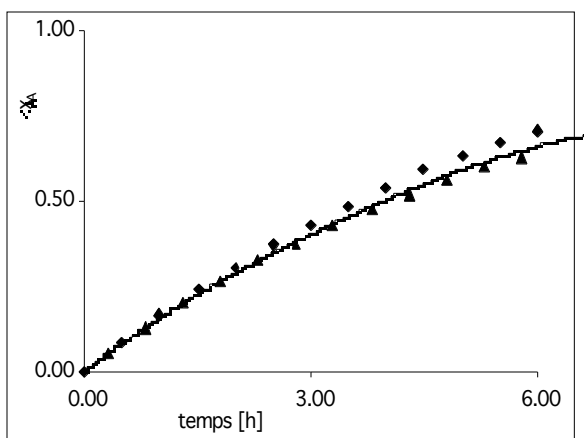


Fig. 9 Comparison between the chemical conversion estimated on-line (solid line), that estimated upon completion of the reaction using calorimeter data ( ) and calculated from the kinetics (▲).

There is a maximum deviation between the three curves of about 5%. The on-line energy balance is in good agreement with the other methods.

Another comparison is possible. In industrial production, the feeding profiles are often kept constant. In order to take into account the safety constraints, the input rate typically implemented is that for which  $T_{cf}$  reaches  $T_{max}$  in just one point. For the experiment considered, the evolution of  $T_{cf}$  for the faster constant input ( $u = 0.043$  l/h) is depicted in Figure 10. Figure 11 shows that an increase of 20% in conversion can be obtained with the proposed method compared to the method generally used in production.

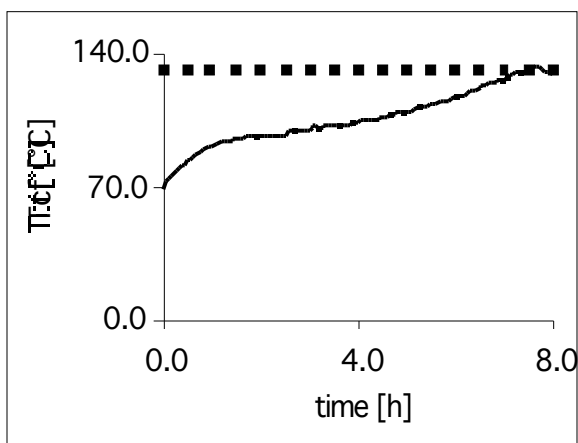


Fig. 10 Evolution of  $T_{cf}$  versus  $T_{max}$  for the faster constant input profile

### 5.3 Limitations of the method

With calorimetric measurements, an error of about 10% on industrial processes can be expected. Indeed, there are many sources of error. Some errors affect the estimates of the heat capacity, the overall heat transfer coefficient or the density. However, the most difficult problem is the on-line evaluation of

Nevertheless, calorimetry is capable of performing the optimisation on-line if, within the safety constraints, one takes into account the sources of error (in  $U$ ,  $c_p$  and  $\rho$ ). For example, instead of  $T_{max}$ , using  $T_{max} - \Delta Ts$  (Eq. 26).

Additionally, as the model does not use the kinetic parameters in the constraint evaluation, the optimization can be performed without any knowledge on the kinetic parameters. Hence, only the initial conditions have to be known with accuracy. In case of doubt on the initial conditions, one has to overestimate the quantities involved in order to overestimate the risk. Hence, one takes a safety margin in case of cooling failure.

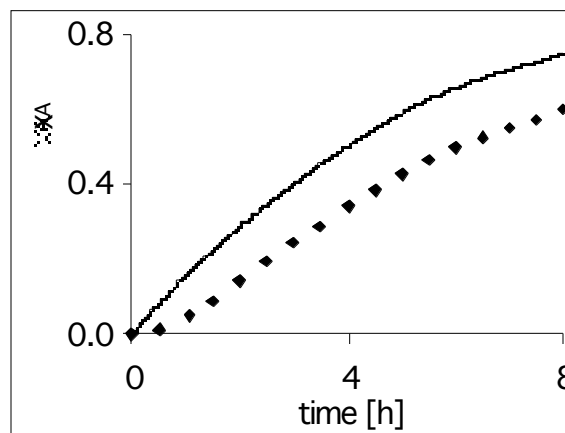


Fig. 11 Comparison of the conversion obtained with the on-line calculated input (solid line) and the constant input (dash line).

## 6. Conclusion

Under safety constraints, on-line optimisation of a second-order reaction performed in a semi-batch reactor has been presented. Calorimetry was used to estimate the extent of reaction and the temperature that results from a cooling failure. The main experimental difficulties were the identification of an accurate base line and the correction for heat effects associated with the feeding.

However, it was shown via comparison of on-line, off-line and simulated results that it is possible to follow the reaction and to determine the optimal feed rate on-line. The main advantage of this method is that, even if the kinetic parameters of the reaction system are unknown, it is possible to increase the productivity without any violation of safety constraints. Moreover, the performance of this method could still improve when used in production because the heat balance is easier to perform at the production scale than at the laboratory scale. Indeed, in production, the heat flow can be evaluated using the temperature difference between the cooling inlet and outlet. Finally, the method proposed helps to increase the chemical conversion in comparison with the constant input profile normally used in production reactors.



### Numerical values of parameters and experimental conditions

Symbol	Description	Value	Unit
$\alpha$	Factor of proportionality	4	
$c_p$	Heat capacity	2000	[J/kg K]
$\Delta H_r$	Reaction enthalpy	-62500	[J/mol]
$\Delta H_{mix}$	Mixing enthalpy	-4200	[J/mol]
$N_A(0)$	Number of moles of A	4	[mol]
$c_{Bin}$	Concentration of B fed	10.7	[mol/l]
$N_B(0)$	Number of moles of B	4	[mol]
$P_1$	Vapor Pressure of the 2-butanol at 54.1 °sC	100	[mmHg]
$\Delta H_{v1}$	Vaporization enthalpy of the 2-butanol	-45.1	[kJ/mol]
$P_2$	Vapor Pressure of the propionic anhydride at 57.7 °C	10	[mmHg]
$\Delta H_{v2}$	Vaporization enthalpy of the propionic anhydride	-49.0	[kJ/mol]
$P_3$	Vapor Pressure of the propionic acid at 65.8 °C	40	[mmHg]
$\Delta H_{v3}$	Vaporization enthalpy of the propionic acid	-46.3	[kJ/mol]
$P_4$	Vapor Pressure of the propionic acid butyl ester at 79.5 °C	100	[mmHg]
$\Delta H_{v4}$	Vaporization enthalpy of the propionic acid butyl ester	-42.4	[kJ/mol]
$\rho_B$	Density of B	808	[kg/m <sup>3</sup> ]
$\Delta T_s$	Safety factor	1	[K]
$T_{in}$	Feed temperature	298	[K]
$T_{max}$	Highest safe temperature	405	[K]
$T_r(0)$	Initial reaction temperature	343	[K]
$\tau$	Sampling time	8	[s]
$U$	Overall heat transfer coefficient	170	[W/m <sup>2</sup> K]
$u_{max}$	Maximum flow rate	$1.42 \cdot 10^{-8}$	[m <sup>3</sup> /s]
$u_{min}$	Minimum flow rate	0	[m <sup>3</sup> /s]
$V_0$	Volume of A	0.61	[l]
$V_{mol}$	Molar volume of 2-butanol	0.091	[l/mol]
$V_{max}$	Maximum volume	0.88	[l]

### Acknowledgement

This work is part of the PhD thesis being prepared at the EPFL by the first author with the financial support of the *Corporate Health, Safety and Environment Department* of Novartis A.G. (Basel). Dr. Eigenmann, head of this Department, is especially thanked.

### References

Abel, O., Marquardt, W., (1998), A model predictive control scheme for safe and optimal operation of exothermic semi-batch reactors. 5<sup>th</sup>

IFAC Symposium on Dynamics and Control of Process Systems. Corfu, Greece.

Arzamendi, G. and Asua, J. M., (1989), Monomer addition policies for copolymer composition control in semicontinuous emulsion copolymerization., J. Appl. Poly. Sci. Vol 38, pp. 2019.

Bou Diab, L., (1999), On-line determination of the global heat transfer coefficient for continuous calibration in chemical and biochemical calorimetry. 9<sup>th</sup> Rc User Forum Europe, October 3-7, 1999, Bern, Switzerland.

Calvet Calorimeter Setaram C80 (1996), User Manual.

Carloff, R., Pross, A., Reichert, K. H., Temperature oscillation calorimetry in stirred tank reactors with variable heat transfer. (1994), Chem. Eng. Technol. Vol. 17, pp. 406-413.

Elvers, B., Hawkins, S. and Russey, W. (Eds.), (1995), Ullmann's Encyclopaedia of Industrial Chemistry, Vol. B8, VCH Verlagsgesellschaft, Weinheim, 5<sup>th</sup> edn.

Galván, I.M., Zaldívar, J.M., Hernández, H., Molga, E., (1996), The use of neural networks for fitting complex kinetic data, Computers Chem. Engng., Vol. 20, pp. 1451-1465.

Gygax, R., (1988), Chemical reaction engineering for safety. Chem. Eng. Sci., Vol. 43, n°8, pp. 1759-1771.

Heinzle, E., Hungerbühler, K., (1997), Integrated process development: the key to future production of chemicals. Chimia Vol. 51, pp. 176-183.

P. Hugo, J. Steinbach and F. Stoessel, (1988), Calculation of the maximum temperature in stirred tank reactors in case of a breakdown of cooling. Chem. Eng. Sci., Vol. 43, n° 8, pp. 2147-2152.

LabView, (1998), National Instruments, User Manual.

Lerena, P., Wehner, W., Weber, H., Stoessel, F., (1996), Assessment of hazards linked to accumulation in semi-batch reactors. Thermochimica Acta. Vol. 289, 127-142

Lim, H. C., Tayeb, Y. J., Modak, J. M. and Bonte, P. (1986), Computational algorithms for optimal feed rates for a class of fed-batch fermentation: Numerical results for penicillin and cell mass production. Biotechnol. Bioeng., Vol 28, pp. 1408-1420.

Marchal-Brassely, S., Villermaux, J., Houzelot, J. L., Georgakis, C., Barnay, J. L., (1989), Une méthode itérative efficace d'optimisation des profils de température et de débit d'alimentation pour la conduite optimale des réacteurs discontinus. Récents progrès en Génie des procédés, Toulouse 1989, Vol. 3 n°9 pp. 441-446.

Nomen, R., Sempere, J. and Serra, E., (1995),

unreacted materials, AFINIDAD LII, Vol. 547, pp. 155-161.

ProMinent (1993), ProMinent Dosiertechnik GmbH, Operating Instructions.

RC1 (1995) Mettler Toledo, Operating Instructions.

Rein, J. A., Phillips, J. A., Yu, K., (1995), Application of Mid IR spectroscopy to bioreactions. 1<sup>st</sup> ReactIR User Forum Europe, October 5-6, 1995, Interlaken, Switzerland.

Regenass, W., (1985), Calorimetric monitoring of industrial chemical processes. *Thermochimica Acta*, Vol. 95, pp. 351-368.

Regenass, W., (1997), The development of stirred-tank heat flow calorimetry as a tool for process optimisation and process safety. *Chimia*, Vol. 51, pp. 189-200.

Sáenz de Buruaga, I., Echevarría, A., Armitage, P. D., de la Cal, J. C., Leiza, J. R., Asua, J. M., (1997), On-line control of a semi-batch emulsion polymerization reactor based on calorimetry. *AIChE J.*, Vol. 43, n°4, pp. 1069-1081.

Schimetzek, R., Giesbrecht, H., (1998), Safe operation of semi-batch reactors by supervising the accumulation of reactants through an on-line energy balance. *Proceeding of the 9<sup>th</sup> International Symposium on Loss Prevention and Safety Promotion in the Process Industries*, May 4-7, 1998, Barcelona, Spain, pp. 523-545.

Schuler, H., Schmidt, C. U., (1992), Calorimetric-state estimators for chemical reactor diagnosis and control: review of methods and applications. *Chem. Eng. Sci.* Vol. 47, n°4, pp. 899-915.

Ubrich, O., Srinivasan, B., Stoessel, F., Bonvin, D., (1999a), Optimization of a semi-batch reaction system under safety constraints. *ECC'99*, 31 August - 3 September 1999, Karlsruhe, Germany.

Ubrich, O., Srinivasan, B., Bonvin, D., Stoessel, F., (1999b), Optimal feed profile for a second order reaction in a semi-batch reactor under safety constraints. *Experimental study. J. Loss Prev. Process Ind.*, Vol. 12, pp. 485-493

Urretabizkaia, A., Leiza, J. R., Asua, J. M., (1994), On-line terpolymer composition control in semicontinuous emulsion polymerization. *AIChE J.*, Vol. 40, n°11, pp. 1850-1864.

Visser, E., (1999), A Feedback-based Implementation Scheme for Batch Process Optimization, Thesis N°2097, Ecole Polytechnique Fédérale de Lausanne, Lausanne, 1999.

Wu, H., Morbidelli, M., Varma, A., (1998), An approximate criterion for reactor thermal runaway. *Chem. Eng. Sci.*, Vol. 53, n°18, pp. 3341-3344.

Wülfert, F., Kok, W., Th., Smilde, A., K., (1998), Influence of temperature on vibrational spectra and consequences for the predictive ability of multivariate models. *Anal. Chem.* Vol. 70, pp. 1761-1767