SAFETY ASSESSMENT AND OPTIMIZATION OF SEMI-BATCH REACTIONS BY CALORIMETRY

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Abstract

Semi-batch reactors are widely spread in the fine chemicals and specialties industry. The reason is that, compared to the pure batch operation, the feed of at least one of the reactants provides an additional way of controlling the reaction course, which represents a safety factor and increases the constancy of the product quality. Process temperature and feed rate can be optimized to satisfy safety constraints, i.e. cooling capacity and allowable accumulation. An economically better way of operating a semi-batch reactor is to adapt the feed rate to the allowed accumulation of reactants. An experimental method based on calorimetry will be presented and illustrated by an example.

Keywords: optimization, process safety, reaction calorimetry, scale-up, semi-batch reactor

Introduction

In the fine chemicals industry, where comparatively small quantities are produced, most of the reactions are performed in discontinuous reactors, which are often equipped as multipurpose units, allowing a flexible operation, the same unit is affected to different processes. This type of practice results also in a different approach of process development, the scale-up becoming an adaptation of the process to some given equipment rather than designing an equipment for a given process. In this frame, the control of the reaction course becomes a concern, which requires quite a lot of efforts during process development. This practice makes the safety evaluation of the process an important task, accompanying the different stages of process development [1].

Compared to the true batch reactor, where all reactants are initially charged to the reactor, the semi-batch reactor or fed-batch reactor presents serious advantages. The feed of at least one reactant allows to control the course of the reaction not only by the temperature control system but also by means of the feed rate. This additional external way of controlling the reactor can be used for safety reasons but may also influence the quality respectively the selectivity of a reaction.

In the industrial practice, a reactor will be considered to be safe if the temperature course can be controlled actively by the heat exchange system during normal operation. There is a second requirement, which is at least as important as the first one: Even if a deviation from these operating conditions occurs, due, for example, to an equipment failure, it shall not lead to a critical situation. A critical situation is a state where the reactor becomes uncontrollable, as, for example, if secondary decomposition reactions are triggered or if the pressure increases provoking the rupture of the reactor.

The basic principles of the safety evaluation of semi-batch reactors will be presented in the first section using a single bimolecular reaction as example to demonstrate some basic methods and concepts. Then, in the second section, a simple procedure to improve the safety of semi-batch processes is presented. A proactive method to improve the productivity, respecting the safety constraints, is presented in the third section and the paper will be summarised in the last section. The paper is focusing on a practical and pragmatic approach of the problem and written in a tutorial style.

Principles of the safety assessment of SBR

With respect to safety two objectives have to be realized. The first is the control of the reaction rate in order to ensure a smooth temperature control even for strongly exothermic reactions. The second objective, which is not always properly recognized, is to limit the accumulation of non-converted reactants in order to limit also the temperature excursion in case of a malfunction. The present paper will emphasize this second objective, which often causes problems, because accumulation is the result of an inappropriate feed rate compared to the reaction rate [2]. Here only homogeneous systems that also represent the worst case with respect to accumulation will be considered.

For a discontinuous exothermic reactions performed in stirred tank reactors, the safety evaluation may be summarized in two key-questions:

- Can the heat of the reaction be removed by the cooling system of the reactor under normal operating conditions?
- Which temperature can be reached in case of a cooling failure and what are the consequences?

These questions and the way how to work out the answers will be illustrated in the following subsections.

Normal operating conditions

Under normal operating conditions, the heat balance of the reactor is governed by the cooling capacity of the reactor. Depending on the temperature control strategy, the conditions can be formulated in different ways. In case of adiabatic reaction, no cooling is required and the normal operating conditions correspond to a cooling failure.

This type of temperature control is used only seldom and for weakly exothermic reactions.

A more common way of the temperature control is the isoperibolic mode, where the temperature of the cooling system is maintained constant, the temperature of the reaction mass is allowed to vary according to the heat release of the reaction. The main problem with this strategy is the possible parametric sensitivity of the reactor, meaning that even small perturbations on the process conditions may lead to dramatic changes, i.e. runaway, in the temperature of the reactor contents. Several authors studied the problem of the parametric sensitivity of semi-batch reactors [3–5]. Original strategies for the identification of potentially hazardous situations and for the control of semi-batch reactors were also developed by different authors [6–9]. These works only consider the problem of the stability under normal operating conditions, i.e. the first question mentioned above.

Beside the adiabatic and the isoperibolic temperature control, a third possibility is the isothermal mode. In the fine chemicals industry modern cascade type temperature controllers allow the isothermal operation which ensures a better reproducibility of the reaction course and consequently of the product quality [10]. For isothermal operation, the cooling capacity of the reactor must exactly compensate the heat released by the reaction at any time. Thus to ensure a safe scale-up of the process, the knowledge of the heat release rate of the reaction performed under conditions which are as close as possible to the future plant conditions is required. A broadly spread way for the implementation of semi-batch reactor is to use a constant temperature and a constant feed rate. For such a type of process calorimetric methods are well adapted to determine the required parameters to ensure safe operation like the maximum heat release rate and the accumulation [11, 12].

Safety after a failure

The second question deals with safety after a deviation from the normal operating conditions. The possible and credible deviations must be identified during a systematic risk analysis of the process. Experiences have shown that the prime causes of runaway incidents are technical failures like agitator or cooling system and undesired side reactions like decomposition reactions [13–15]. In this context, semi-batch processes present a definitive advantage over batch processes in the sense that processes can be designed to remain safe, even in the case of an equipment failure, by limiting the accumulation of the non-converted material. This means that the design procedure must also incorporate safety aspects [16], especially the reduction of the energy potential that could be released in an uncontrolled way in case of a failure. This represents an important step towards inherently safer processes [17].

The question of stability was considered together with a failure scenarios by Abel and Marquardt who introduced a model predictive control scheme allowing to maintain the accumulation within safe borders [18]. The drawback of this method is that a detailed knowledge of the reaction kinetics is required. This point is especially critical for industrial applications, where the kinetic parameters are generally not

known in detail, but some rough ideas on the reaction scheme are often available. It is the aim of this work to present a methodology for the safety assessment and for the design of safe semi-batch processes with reduced kinetic information.

Reaction calorimetry for a safety evaluation

Reaction calorimetry is a powerful tool for this task, because it allows to perform a reaction under conditions close to those that will be used at industrial scale [19–23], which is essential for scale-up purposes. Moreover reaction calorimetry allows to determine essential parameters for process development purposes and chemical engineering [11, 24].

A general approach of a safety study for a semi-batch reactor, in the frame of scale-up will be illustrated by the example of a single bimolecular second order reaction, followed by a decomposition reaction. The process must be scaled up to an industrial reactor of 4 m^3 nominal volume. The reaction scheme is: A+B→P→S, where the first reaction is overall second order, i.e. first order in each reactant. The decomposition reaction is first order in P. The physical chemical and kinetic data of the reaction system are summarized in Table 1 together with those of the industrial reactor. It is important to notice that the kinetic data will never be explicitly used in the solution of the problem, i.e. their knowledge is not required.

Table 1 Data used for the simulation

| Reaction data	Decomposition reaction	Reactor data
$\Delta H_R = -200$ kJ mol^{-1}	$\Delta H_R = -500$ kJ mol^{-1}	$V_0 = 3$ m^3
$E_a = 60$ kJ mol^{-1}	$E_a = 100$ kJ mol^{-1}	$V_f = 4$ m^3
$k_\infty = 10^9$ kg (mol h)$^{-1}$	$k_\infty = 5 \cdot 10^{10}$ h^{-1}	$A = 7.4$ m^2
$C_p = 1.7$ kJ (kg K)$^{-1}$		$U = 150$ W (m^2 K)$^{-1}$
$C_{A_0} = 2$ mol kg^{-1}		$T_{cool} = 30°C$
$M = 1.2$		
$\rho = 1000$ kg m^{-3}		

The following curves were obtained by numerical simulation using Madonna © 1997–1998 R. I. Macey and G. F. Oster. The reaction calorimetric experiment is supposed to be performed in a Mettler RC1 calorimeter using the conditions for the large-scale equipment: the temperature is 60°C for a feed at constant rate during 5 h.

The results (Fig. 1), directly deliver the maximum heat release rate of about 15 W kg^{-1}. This value can be compared to the cooling capacity of the plant equipment, which is in the range of ca 10 W kg^{-1} at the beginning of the reaction using the data in Table 1. Thus the cooling capacity will be insufficient to maintain isothermal conditions at plant scale. Further, by integration of the heat release rate one obtains the heat of reaction of 300 kJ kg^{-1} and the conversion curve. The feed has been normalized to the stoichiometry since an excess of 20% has been added (Fig. 2). This al-

lows calculating the accumulation as the difference between the feed (up to 100%) and the thermal conversion. This is the basis of the calculation of the MTSR:

$$\text{MTSR} = T_p + \left(X_{acc,max} \Delta T_{ad} \frac{M_{Rf}}{M_{R,max}} \right)$$

with M_{Rf} mass of reaction mixture at end of feed (4000 kg), $M_{R,max}$ mass of reaction mixture at stoichiometric point (3833 kg).
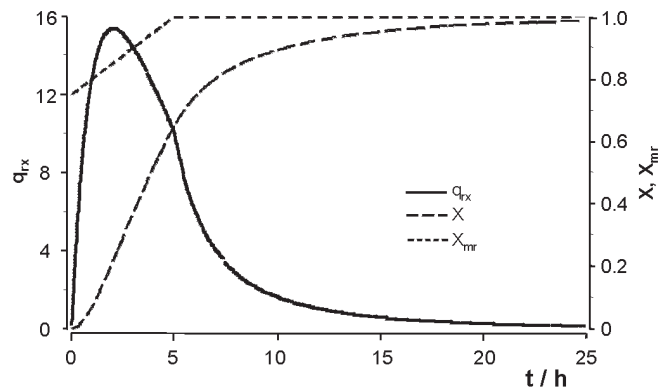
Fig. 1 Result of the reaction calorimeter experiment, heat release rate of the reaction, thermal conversion and feed
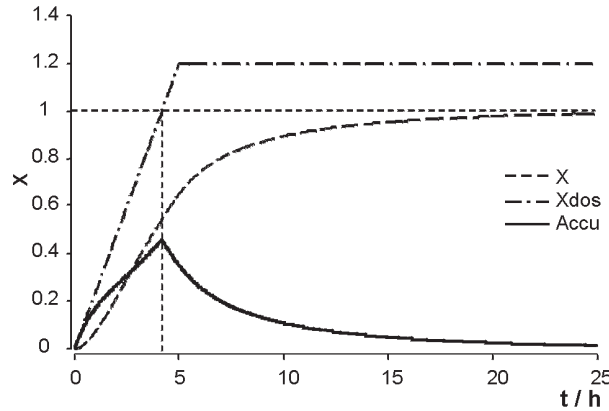
Fig. 2 Result of the reaction calorimeter experiment, feed normalized at stoichiometry, thermal conversion and accumulation

In our example, the MTSR of 148°C is reached in case of a failure at after a feed time of 4.17 h, i.e. at the stoichiometric point (Fig. 3). Thus the consequences of a cooling failure would be a fast temperature increase up to about 150°C.

The pressure of the system at this temperature and the thermal stability can be evaluated now. This last point, i.e. the thermal stability of the reaction mixture, can be
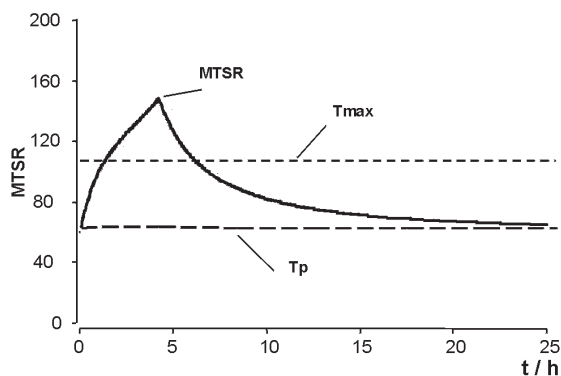
Fig. 3 Evaluation of the reaction calorimeter experiment, calculation of the MTSR

characterized by the time to maximum rate under adiabatic conditions (TMRad), which gives an idea of the time left to take measures to avoid the runaway of the decomposition reaction [25]. The data used for the example presented here are summarized in Table 2. Below 110°C, a reasonable time is left to take counter measures, thus 110°C will be considered as the maximum allowed temperature with respect to the thermal stability of the reaction mixture. This temperature allows to ensure a TMRad of approx. 20 h, which is the generally used criterion.

Table 2 Thermal stability of the final reaction mass

$T/°C$	90	95	100	105	110	115
$q_{max}/W\ kg^{-1}$	0.05	0.08	0.12	0.18	0.27	0.40
TMRad/h^{-1}	110	70	47	31	22	15

Hence, starting from the MTSR 150°C, a cooling failure would definitely lead to a critical situation: the thermal explosion would take place within minutes. The process must be assessed to be very critical.

Improving the process safety

The example process presents two major problems: (i) the heat release rate of the reaction is too high compared to the available cooling capacity and (ii) the accumulation of non-converted reactants may lead to a thermal explosion in case of cooling failure. Reducing the heat release rate can only be achieved by dilution or by reducing the reaction rate, for example by decreasing the feed rate. Since the accumulation is the result of a discrepancy between feed rate and reaction rate it can also be reduced by decreasing the feed rate. Hence the feed rate is an important design factor for semi-batch operations [26]. In Figs 4 and 5 the effect of the feed rate, expressed as feed time, on the heat release rate and on the MTSR is shown. The feed rate is maintained constant during the feed time.

The drawback of these solutions is an important increase of the cycle time, meaning a loss of productivity that is not compatible with the economy of the process. The time required to achieve 95% conversion is over 21 h. Thus a better solution is to try to increase the process temperature: this increases the available temperature difference with the cooling system linearly and the reaction rate exponentially, reducing the accumulation by the same way. This temperature increase can be driven up to a level where, even with a low accumulation, the initial temperature is too high to ensure the thermal stability of the reaction mass. This effect is shown in Fig. 6: the reaction was performed at 60, 90 and 120°C and a cooling failure was simulated, starting at 4.17 h, when the stoichiometric point is reached.
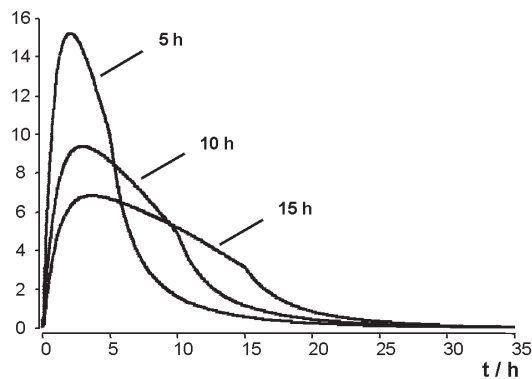

Fig. 4 Effect of the feed rate on the heat release rate, feed time 5, 10 and 15 h
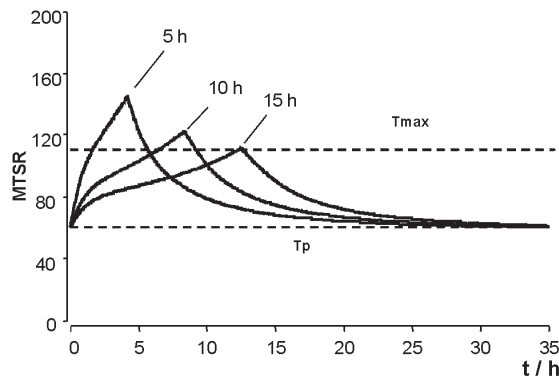

Fig. 5 Effect of the feed rate on the MTSR, feed time 5, 10 and 15 h

The maximum heat release rate is 23 W kg^{-1} at 90°C and 26 W kg^{-1} at 120°C. At 90°C the cooling capacity of the industrial reactor is 22 W kg^{-1} which is somewhat too low. At 120°C, the cooling capacity is 33 W kg^{-1} which is fairly above the required capacity. But at this temperature, even with the reduced accumulation, the runaway of the decomposition reaction would occur some 3 h after the cooling failure.
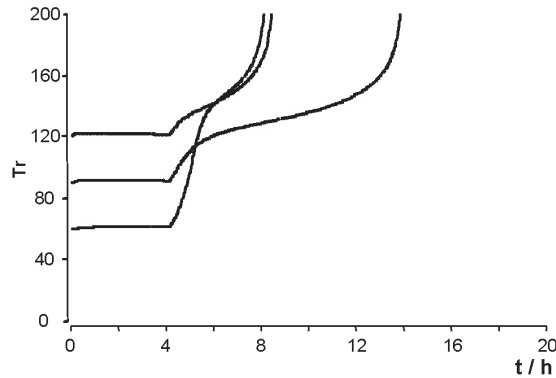
Fig. 6 Temperature course after a cooling failure at the instant of maximum accumulation with 3 different process temperatures: 60, 90 and 120°C, with a feed time of 5 h, the failure occurring at 4.17 h

At the lower temperature, the accumulation is so large, that on malfunction the runaway immediately leads to a temperature range where the secondary decomposition reaction also runs away very fast. At the opposite, a too high reaction temperature, if the desired reaction proceeds with a very small accumulation, in case of malfunction, the initial temperature level is so high that the secondary reaction immediately takes a runaway course [27]. The optimum temperature chosen in this example allows to stabilize the temperature at an intermediate level, where enough time is available to take counter measures (emergency cooling, dumping, flooding etc.) [25].
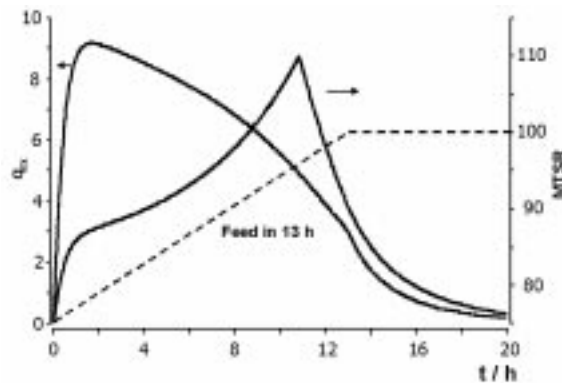
Fig. 7 Curve of a process respecting the constraints: heat release rate and MTSR

A possible process respecting both constraints, the cooling capacity and the MTSR is a temperature of 75°C with a constant feed rate during 13 h. Such a curve is presented in Fig. 7.

This process fulfills the safety criteria and the time required to achieve 95% conversion was reduced to 14.2 h

Improvement of the productivity by modulation of the feed

Principles of the method

When looking at the MTSR-curve in Fig. 7, one immediately notices, that the maximum allowed temperature is just reached at one point, namely at the stoichiometric point. This also means that, especially during the beginning of the reaction before the stoichiometric point, the process could tolerate a higher accumulation. This is equivalent to a higher concentration of B and consequently to a higher reaction rate. Hence a higher accumulation would improve the productivity. After the stoichiometric point, the accumulation of B plays no more any role, since it is in stoichiometric excess. At this stage the accumulation is driven by the concentration of A, which was initially charged to the reactor and thus cannot be influenced by the feed. Consequently, the remaining B (the stoichiometric excess) could be added much faster, without creating any risk in case of a failure.
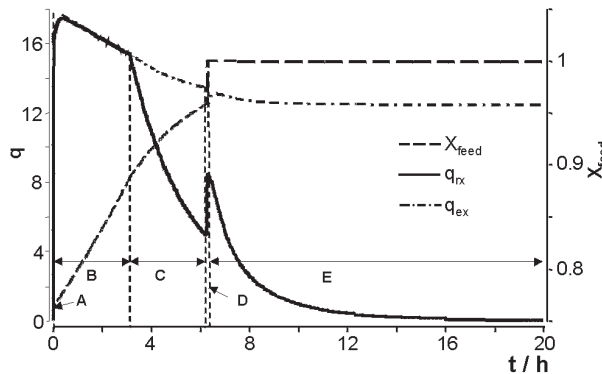

Fig. 8 Reaction with modulated feed. Heat release rate of the reaction and feed

In an ideal way, the addition should be controlled in such a manner that the rate is maximum. But there are three constraints on the addition rate: (i) the heat release rate must stay below the cooling capacity, (ii) the accumulation must stay below a critical level defined by the MTSR relative to the maximum allowed temperature, (iii) the feed rate is physically limited. Such a process is presented in Fig. 8. In a first very short period of time, the feed is at its maximum rate until the constraint of the cooling capacity is reached (Period A). Then the feed rate is adapted to the cooling capacity (Period B) until the accumulation becomes too important (Period C). After the stoichiometric point, the feed rate is again at its maximum value (Period D).

The increase in productivity can be evaluated by comparing the conversion curves (Fig. 9). With the traditional process the conversion of 95% is reached after 14.2 h, whereas with the modulated feed it is reached within 8.9 h. This represents a gain of over 37%, which will shorten the cycle time in an interesting way.

It can be shown that this type of feed control leads to an optimum productivity if the system is feedback linearizable [28]. This mathematical property depends essen-
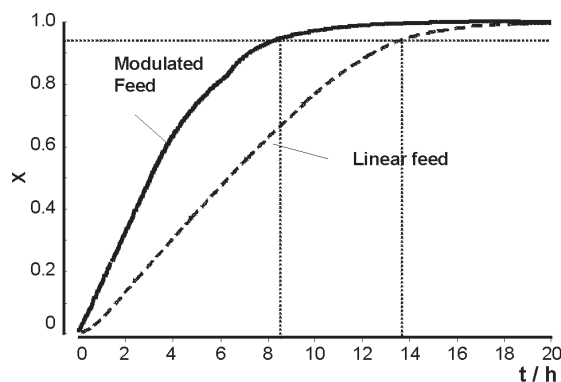
Fig. 9 Comparison of optimized process with constant feed rate and modulated feed rate

tially on the structure of the differential equations, which describe the system. This property was analyzed for some common systems [29], the results are summarized in Table 3. In fact for all these systems, the productivity would be maximum in the true batch reactor, but in the batch mode, the safety of those processes could not be achieved.

Table 3 Feedback linearizable systems

Reaction type	Reaction scheme		Feedback linearizable
Single bimolecular	A+B→P		yes
Competition with same order	A+B→P A+B→S	same order	yes
Consecutive reactions (product decomposes)	A+B→P→S		yes
Competition with different order	A+B→P A+B→S	different order	no
Competition with product	A+B→P A+P→S	competitive consecutive	yes
Feed decomposes	A+B→P B→S	feed decomposes	no
Impurity in feed	A+B→P A+C→S	impurity in feed	yes

For feedback linearizable systems, the optimum with respect to productivity and safety lies on the constraints. Or in a more 'chemically oriented' language the following rule can be given: For reactions having their highest productivity in the true batch mode, the optimum feed must maintain the system at the safety constraints i.e. maximum allowed heat release rate or maximum allowed accumulation.

This also means that it is sufficient to know the structure of the rate equations without knowing the exact kinetic parameters i.e. the frequency factors and activation

energies. Since these considerations were only a 'green desk' approach, the method will be illustrated by an experiment.

Experimental realization

In order to be able to verify that the optimum is really reached, a reaction with known kinetic parameters was selected. The test reaction was the esterification of propionic anhydride with 2-butanol. This reaction is known to be bimolecular second order i.e. first order in each reactant under the conditions used here [30]. A first possibility is to implement an off-line control (open-loop control), but this procedure requires the knowledge of the kinetic parameters of the reaction [31]. Such an approach of process control, does not allow to verify if the process really remains on the desired tracks. For this reason a closed loop controller, allow a feedback was implemented. This implies tracking of the accumulation to use this information to control the addition rate of the reactant.
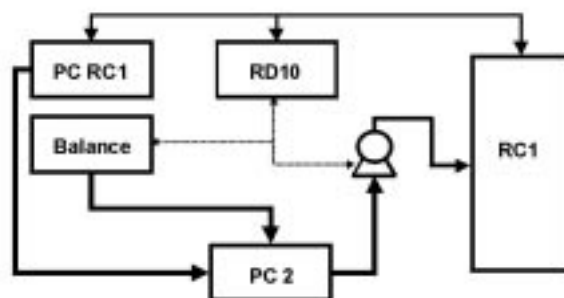

Fig. 10 Schematic view of the equipment

The method presented above presupposes that the constraints can be evaluated instantaneously at all times. On the one hand, the constraint associated with the normal operating conditions (the heat release rate of the reaction must be inferior to the cooling capacity) can be evaluated by calorimetry. On the other hand, the constraint arising from a hypothetical cooling failure can also be evaluated from calorimetric data as soon as the thermal accumulation can be estimated. With commercially available software for the reaction calorimeter, it is not possible to calculate the constraints on-line, hence it is not possible either to evaluate the optimal feed rate on-line. Thus an external computer and associated programs are used to perform the on-line heat balance calculations and control the addition of reactant. A schematic view of the equipment based on a Mettler-RC1 is presented in Fig. 10.

The reaction was run isothermally at 70°C and the feed controlled by the on-line heat balance. The MTSR-curve (Fig. 11) and the conversion curves (Fig. 12) compared with the theoretical one show that the objective was reached with a very good agreement [29].
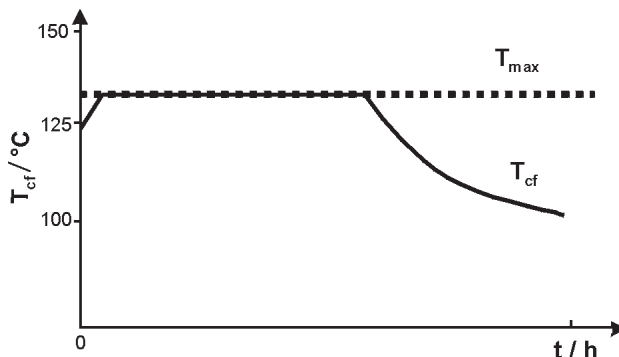
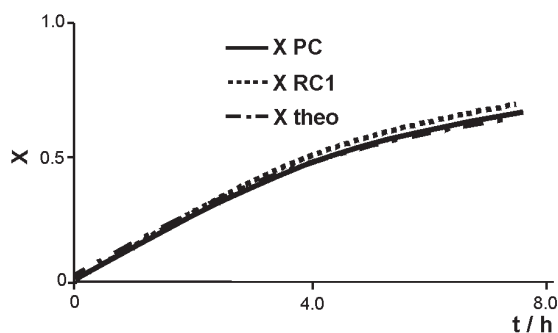**Fig. 11** MTSR as a function of time with modulated feed

Fig. 12 Conversion curves

It was also verified, by experimental simulation of a cooling failure (setting the calorimeter to adiabatic mode) that the constraints are really respected. The on-line heat balance was implemented on a Mettler RC1 Reaction calorimeter, but it can be implemented on industrial reactors as well. In this case the heat balance could be obtained by measuring the flow rate and the temperature increase of the heat exchange fluid.

Conclusions

It was shown how reaction calorimetry can be used to evaluate the safety of semi-batch processes. This evaluation was performed without any explicit knowledge of the kinetic parameters of the reaction. The assessment essentially answers two questions:

- Can the reaction temperature be controlled under normal operating conditions (scale-up)?
- What would the consequences of a cooling failure be?

Furthermore, the process temperature and feed rate can be optimized to satisfy the safety constraints, i.e. the cooling capacity and the allowable accumulation: the

maximum accumulation is just reached at the stoichiometric point for single bimolecular reactions.

An economically better way of operating a semi-batch reactor is to adapt the feed rate to the allowed accumulation of reactants. This implies to be able to track the accumulation during the reaction and to use this information to control the addition rate of the reactant. An experimental method based on calorimetry has been presented and illustrated by an example. The method can also be used in industrial reactors and can be extended to more complex reaction kinetics. It still increases the performance of the reactor while strictly maintaining a safe operation even in case of malfunction of the equipment.

A systematic methodology for the development of this type of operation was presented, allowing to identify the processes where this technique can be applied. Only the structure of the rate equations and not the value of the rate constants is required in this method. This represents the strength of the approach. By combining the optimization of the productivity with the constraint of safety, it represents a useful tool in the frame of development of inherently safer processes.

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