Safety Assessment and Optimization of Semi-Batch Reactions by Calorimetry

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INTRODUCTION

- **In the fine Chemicals industry**
  - comparatively small quantities are produced
  - most of the reactions are performed in discontinuous reactors
  - often equipped as multipurpose units, allowing a flexible operation

- **This type of practice**
  - results in a different approach of process development
  - the scale-up becoming an adaptation of the process to given equipment rather than designing an equipment for a given process
  - the control of the reaction course becomes a concern, which requires quite a lot of effort during process development
  - make the safety evaluation of the process an important task

INTRODUCTION

◆ **Semi-batch reactors are widely spread in the fine chemicals industry**

- 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 (cooling capacity, allowable accumulation)

- An experimental method based on calorimetry will be presented and illustrated by an example

INTRODUCTION

- A reactor will be considered to be safe if the temperature course can be controlled actively by the heat exchange system during normal operation
- 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

Principles of the safety assessment of SBR

- **With respect to safety two objectives have to be realized**

  - the control of the reaction rate in order to ensure a smooth temperature control even for strongly exothermic reactions

  - to limit the accumulation of non converted reactants in order to also limit the temperature excursion in case of a malfunction

accumulation is the result of an inappropriate feed rate compared to the reaction rate

Principles of the safety assessment of SBR

- **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?

Nomal Operating Condition

◆ 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
- the normal operating conditions correspond to a cooling failure
- This type of temperature control is used only in seldom cases and for weakly exothermic reactions

Nomal Operating Condition

- **A more common way of temperature control is the isoperibolic mode**
  - The temperature of the reaction mass being allowed to vary according to the heat release of the reaction
  - The main problem : the possible parametric sensitivity of the reactor

even small perturbations on the process conditions may lead to dramatic changes, i.e. runaway, in the temperature of the reactor contents

Normal Operating Condition

◆ **In case of isothermal mode**

- fine chemicals industry modern cascade type temperature controllers allow the isothermal operation
- Ensure a better reproducibility of the reaction course and consequently of the product quality
- The cooling capacity of the reactor must exactly compensate the heat released by the reaction at any time
- To ensure a safe scale-up of the process, the knowledge of the heat release rate of the reaction is required
- calorimetric methods are well adapted to determine the required parameters to ensure safe operation like the maximum heat release rate and the accumulation

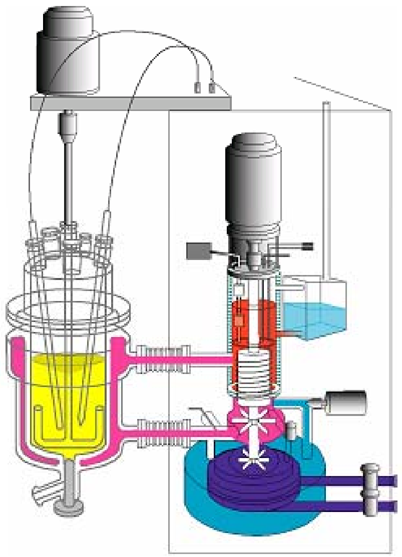
Safety after a failure

- 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
  - Experience has shown that the prime causes of runaway incidents are technical failures like agitator or cooling system and unwanted side reactions like decomposition reactions
- Processes can be designed to remain safe, even in the case of an equipment failure, by limiting the accumulation of non converted material
- 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**

- it allows performing a reaction under conditions close to those that will be used at industrial scale, which is essential for scale-up purposes
- it allows determining essential parameters for process development purposes and chemical engineering



Reaction calorimetry for a safety evaluation

- **Methodology**
  - 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 $\rightarrow$ P $\rightarrow$ S where the first reaction is overall second order. The decomposition reaction is first order in P

Reaction calorimetry for a safety evaluation

- The physical chemical and kinetic data of the reaction system

Table 1: Data used for the simulation

Reaction Data	Decomposition reaction	Reactor data
ΔH_R = -200 kJ/mol Ea = 60 kJ/mol $k_\infty = 10^9$ kg/(mol.h) Cp' = 1.7 kJ/(kg.K) CA_0 = 2 mol/kg M= 1.2 ρ= 1000 kg/m^3	ΔH_R = -500 kJ/mol Ea = 100 kJ/mol $k_\infty = 5.\ 10^{10}\ h^{-1}$	$V_0 = 3\ m^3$ V_f= 4m3 A= 7.4 m^2 U= 150 W/(m^2.K) T_{cool} = 30 °C

- The reaction calorimetric experiment is supposed to be performed in a RC1 calorimeter using the conditions for the large scale equipment
- the temperature is 60 ℃ for a feed at constant rate during 5 hrs

Reaction calorimetry for a safety evaluation

◆ **Result of the reaction calorimeter experiment(1)**

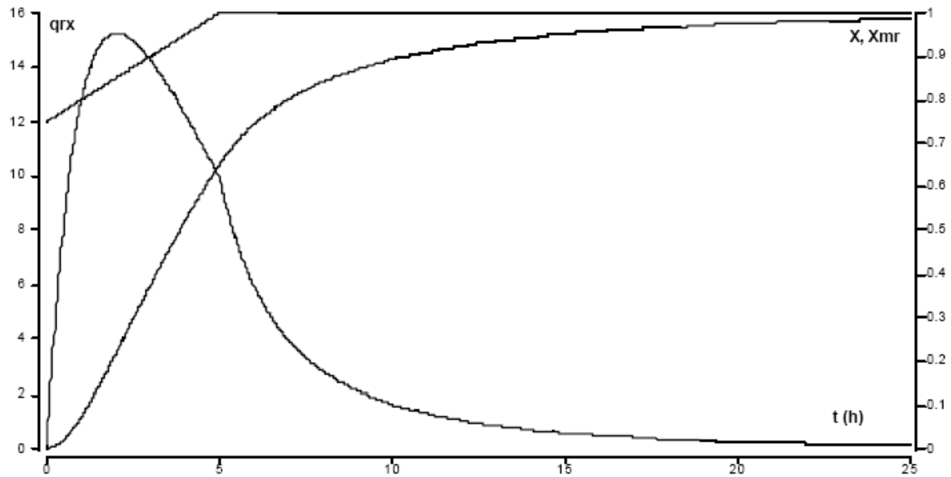


Fig. 1: Result of the reaction calorimeter experiment, heat release rate of the reaction, thermal conversion and feed.

- maximum heat release rate : about 15 W/kg
- cooling capacity of the plant equipment : about 10 W/kg
- cooling capacity : insufficient to maintain isothermal conditions at plant scale
- obtain heat of reaction of 300 kJ/kg and the conversion curve

Reaction calorimetry for a safety evaluation

◆ **Result of the reaction calorimeter experiment(2)**

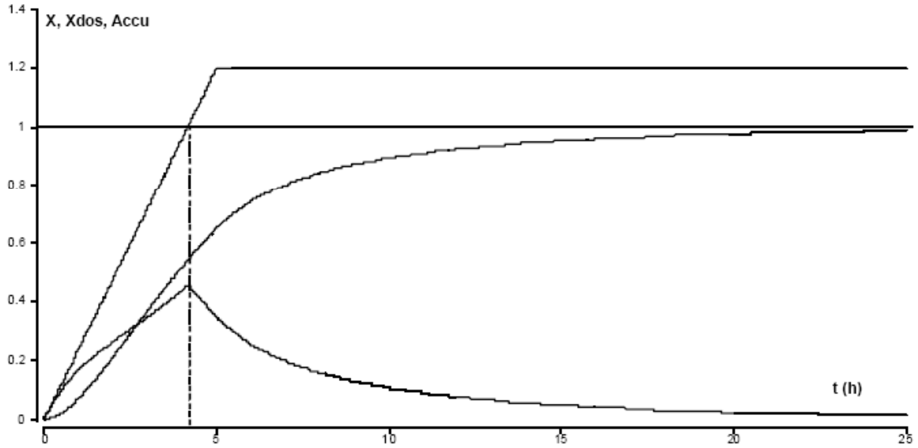


Fig. 2: Result of the reaction calorimeter experiment, feed normalized at stoichiometry, thermal conversion and accumulation.

- heat of reaction and conversion has been normalized to the stoichiometry since an excess of 20 % has been added
- This allows calculating the accumulation as the difference between the feed (up to 100%) and the thermal conversion

Reaction calorimetry for a safety evaluation

◆ **Basis of calculation of the MTSR (from Results of RC experiment)**

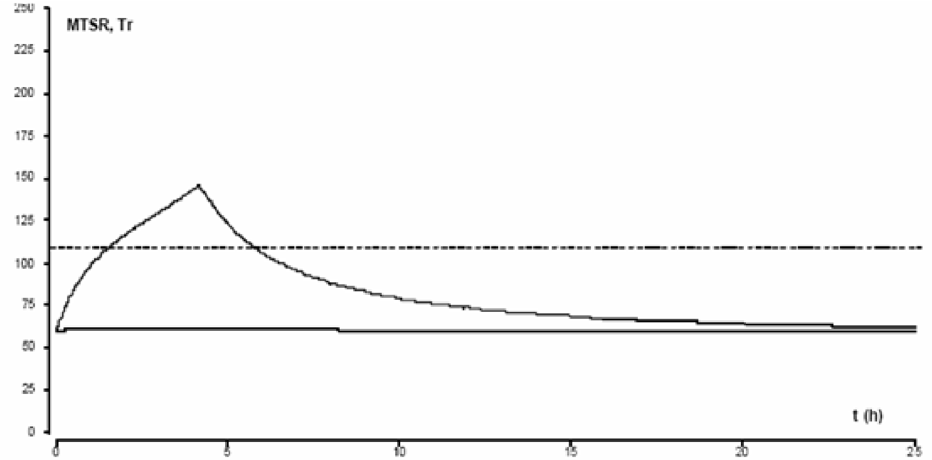


Fig 3: Evaluation of the reaction calorimeter experiment, calculation of the MTSR.

$$MTSR = T_p + X_{acc,max} \cdot \Delta Tad \cdot M_{Rf} / M_{R\,max}$$

M_{Rf}	Mass of reaction mixture at end of feed (4000 kg)
$M_{R,max}$	Mass of reaction mixture at stoichiometric point (3833 kg)

- The MTSR of 148 ℃ is reached in case of a failure at after a feed time of 4.17 hrs, i.e. at the stoichiometric point.
- The consequences of a cooling failure would be a fast temperature increase up to about 150 ℃.

Reaction calorimetry for a safety evaluation

◆ **The pressure of the system at this temperature and the thermal stability**

- The thermal stability of the reaction mixture can be characterized by the Time to Maximum Rate under adiabatic conditions (TMR_{ad})
- TMR_{ad} gives an idea of the time left to take measures to avoid the runaway of the decomposition reaction
- Thermal stability of the final reaction mass

Table 2: Thermal stability of the final reaction mass.

T (°C)	90	95	100	105	110	115
qmax (W/kg)	0.05	0.08	0.12	0.18	0.27	0.40
TMRad (h)	110	70	47	31	22	15

- This temperature allows ensuring a TMR_{ad} of approx. 20 hours, which is the generally used criterion

Reaction calorimetry for a safety evaluation

- 110 ℃ will be considered as the maximum allowed temperature with respect to the thermal stability of the reaction mixture

◆ Starting from the MTSR = 150 ℃, 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**
  - the heat release rate of the reaction is too high compared to the available cooling capacity
  - the accumulation of non converted reactants may lead to a thermal explosion in case of cooling failure
- Reducing the heat release rate can be achieved 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

The feed rate is an important design factor for semi-batch operations

Improving the process safety

◆ Effect of the feed rate on the heat release rate and MTSR, feed time 5, 10 and 15 h (feed rate : constant)

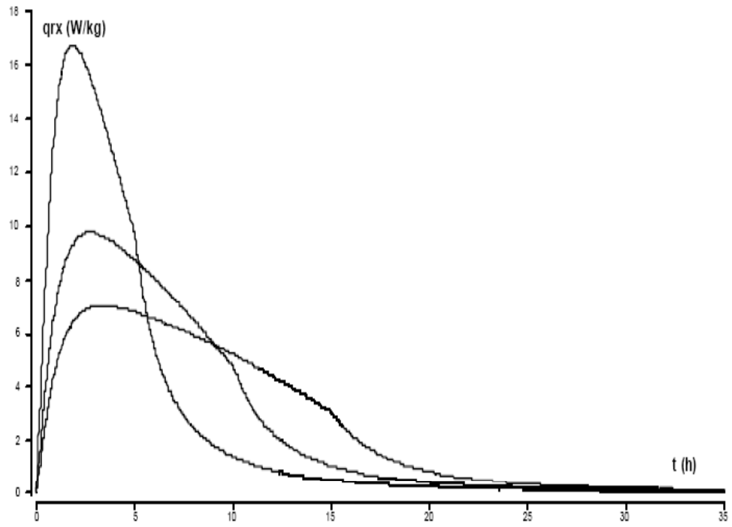


Fig. 4: Effect of the feed rate on the heat release rate, feed time 5, 10 and 15 hrs.

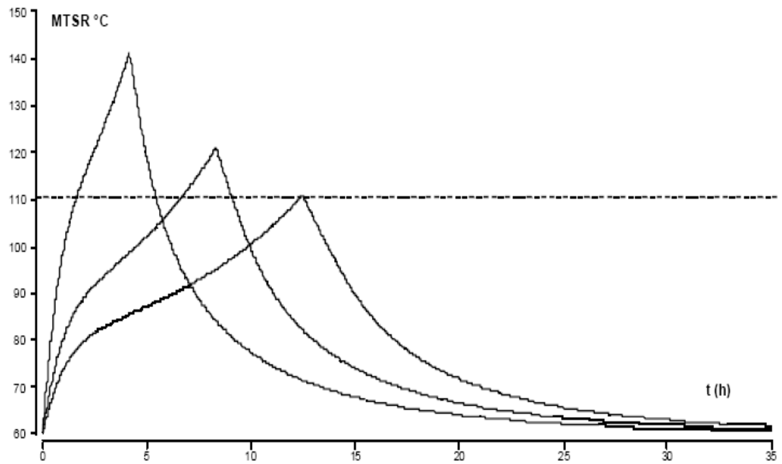


Fig. 5: Effect of the feed rate on the MTSR, feed time 5, 10 and 15 hrs.

➢ The draw back 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 (95 % conversion : 21 h)

Improving the process safety

- **A better solution is to try to increase the process temperature**
  - increase 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 the initial temperature is too high to ensure the thermal stability of the reaction mass

Improving the process safety

◆ Temperature course after a cooling failure at the instant of maximum accumulation with 3 different process temperatures

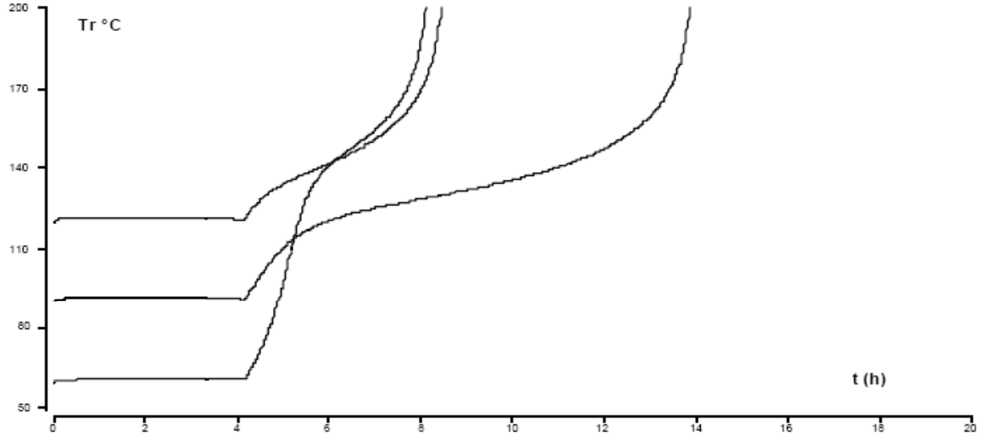


Fig.6: Temperature course after a cooling failure at the instant of maximum accumulation with 3 different process temperatures: 60, 90 and 120 °C, with a feed time of 5 hrs, the failure occurring at 4.17 hrs

- maximum heat release :
  15 W/kg(60 ℃)
  23 W/kg(90 ℃)
  26 W/kg(120 ℃)

- cooling capacity : 10 W/kg(60 ℃), 22 W/kg(90 ℃), 33 W/kg(120 ℃)
- at 120 ℃, the runaway of the decomposition reaction would occur some 3 hours after the cooling failure (with the reduced accumulation)

Improving the process safety

- 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 high temperature, if the desired reaction proceeds with very small accumulation, in case of malfunction, the initial temperature level is so high that the secondary reaction immediately takes a runaway course

- The optimum temperature allows to stabilize the temperature at an intermediate level, where enough time is available to take counter measures (emergency cooling, dumping, flooding etc.)

Improving the process safety

- ◆ A possible process respecting both constraints, the cooling capacity and the MTSR is a temperature of 75 ℃ with a constant feed rate during 13 h

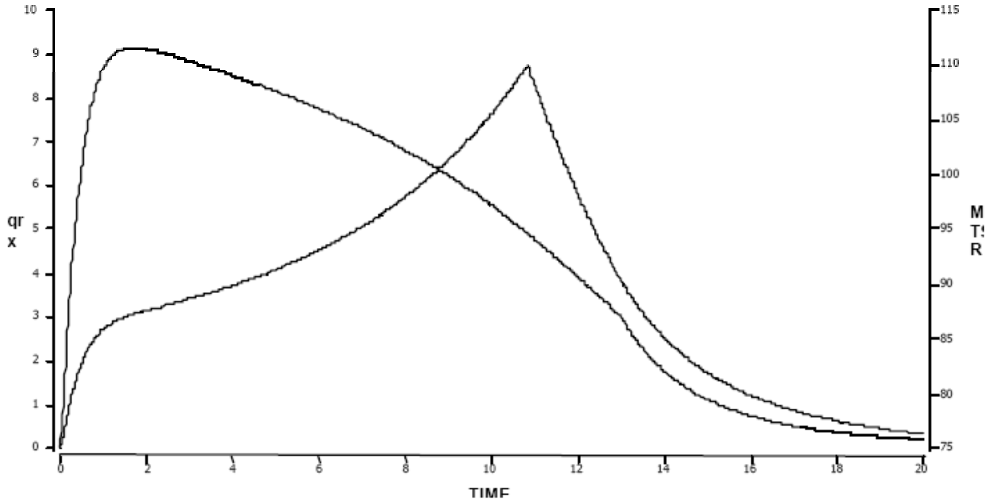


Figure 7: Thermogramm of a process respecting the constraints. The heat release rate of the reaction and the MTSR are shown.

  - ➢ 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

◆ **Principles of the method**

- the maximum allowed temperature is just reached at one point, namely at the stoichiometric point
- during the beginning of the reaction before the stoichiometric point, the process could tolerate a higher accumulation
- a higher accumulation would improve the productivity ($C_B \uparrow \rightarrow r \uparrow$)
- After the stoichiometric point, the accumulation of B plays no more any role, since it is in stoichiometric excess ➡ the accumulation is driven by the concentration of A (Initially charged to the reactor)

⬇

Consequently the remaining B (the stoichiometric excess) could be added much faster, without creating any risk in case of a failure.

Improvement of the productivity by modulation

- **three constraints on the addition rate**
  - the heat release rate must stay below the cooling capacity
  - the accumulation must stay below a critical level defined by the MTSR relative to the maximum allowed temperature
  - the feed rate is physically limited

Improvement of the productivity by modulation

◆ Reaction with modulated feed

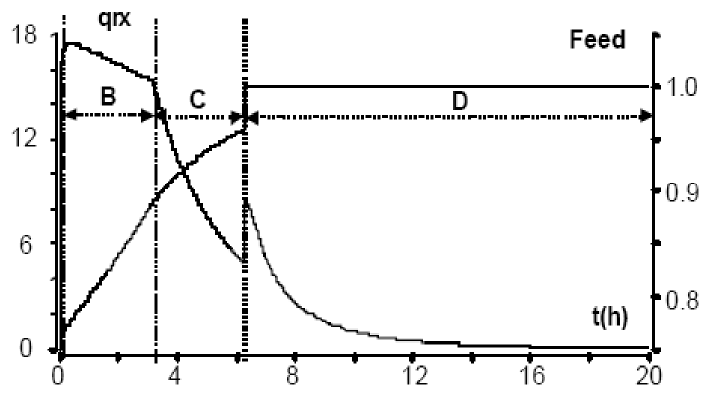


Fig. 8: Reaction with modulated feed. Heat Release rate of the reaction, and feed.

- the feed is at its maximum rate until the constraint of the cooling capacity is reached (Period A)
- 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)

Improvement of the productivity by modulation

◆ comparison of optimized process with constant feed rate and modulated feed rate

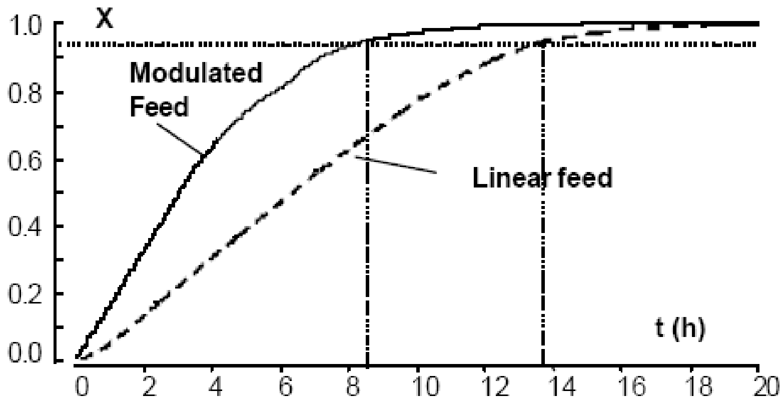


Figure 10: Comparision of optimized process with constant feed rate and modulated feed rate: conversion.

- with the traditional process the conversion of 95% is reached after 14.2 h
- with the modulated feed the conversion of 95% is reached within 8.9 h
- this represents a gain of over 37%, which will shorten the cycle time in an interesting way.

Improvement of the productivity by modulation

◆ Experimental realization

- 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

conclusion

- 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 be the consequences of a cooling failure?
- the process temperature and feed rate can be optimized to satisfy the safety constraints
  - the cooling capacity and the allowable accumulation

conclusion

- 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
  - The method can also be used in industrial reactors and can be extended to more complex reaction kinetics

- 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