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## Assessment of hazards linked to accumulation in semi-batch reactors<sup>1</sup>

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### Abstract

In the assessment of hazards linked to chemical reactions, two aspects must be considered: the behavior of the reactor under normal operating conditions, i.e. the controllability of the reaction rate and the behavior in case of failure. The maximum temperature which can be attained in the case of a cooling failure by an exothermic synthesis reaction (MTSR) is a parameter of great significance for the assessment of the thermal safety of semi-batch reactions. This temperature depends on the accumulation of non-converted reactants at the instant of the failure. In most cases, the determination of MTSR is possible after one experiment performed in a reaction calorimeter following standard operating procedures. Such an experiment allows the evaluation of the heat of accumulation as a function of time during addition of reactants. However in some cases, with multiple reactions, another experimental approach, including simulation of the failure and coupling of spectroscopic methods, has to be used. Examples will illustrate the determination of the MTSR in such more difficult cases.

*Keywords:* Maximum temperature of synthesis reaction; Reaction calorimetry; Thermal safety

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### 1. Introduction

The concept of the Maximum Temperature of Synthesis Reaction (MTSR) was first developed by Gyax [1], together with the cooling failure scenario, within the framework of the assessment of thermal risks of chemical processes. Today, it is widely used by different companies for their risk evaluations [2,3]. For single second-order

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reactions performed in a semi-batch reaction, a detailed method was recently published [4]. For more complex reactions, different strategies have to be used. The aim of this paper is to show some examples of more complex reactions, stemming from the practice of our safety laboratory.

### 1.1. The MTSR concept

The Maximum Temperature of Synthesis Reaction (MTSR) is the temperature reached by the reaction mixture if the energy potential of the solely desired reaction is released under adiabatic conditions. This temperature is used to predict whether the loss of control of a desired reaction can trigger an undesired decomposition reaction [5,6]. Here, only the heat of the desired (synthesis) reaction is considered. Of course, the temperature level, which can be reached in the case of a cooling failure ( $T_{cf}$ ), is a function of the process temperature ( $T_R$ ) of the amount of non-converted material present in the reactor (that is, the degree of accumulation  $X_{ac}$ ) and of the total adiabatic temperature rise ( $\Delta T_{ad}$ ) [7, 12].

$$T_{cf} = T_R + X_{ac} \Delta T_{ad} \quad (1)$$

The degree of accumulation is the fraction of the total heat of reaction which has not yet been released

$$X_{ac} = 1 - \frac{\int_0^t q_{rx}(t) dt}{\int_0^\infty q_{rx}(t) dt} \quad (2)$$

where  $q_{rx}(t)$  is the heat release rate of the desired reaction

The accumulation may vary with time during the reaction. Thus, the knowledge of the instant at which it is at a maximum is an important datum for the prediction of the behavior of a reactor in the case of a cooling failure. The assessment of the process safety and the design of safety measures is based on the MTSR which corresponds to the maximum  $T_{cf}$

$$\text{MTSR} = [T_{cf}]_{\max} \quad (3)$$

### 1.2. Limitations

The standard procedure to determine the MTSR involves the estimate from a single RC experiment of the heat that can be released after all the reactants are present in the reaction medium in stoichiometric amounts. The principle of measurement for a semi-batch process involves a reaction calorimetry experiment under the normal operating conditions of the reaction, which allows determination of the thermal conversion and accumulation as a function of time. The MTSR is calculated from Eqs. (1–3).

This method presents limitations in the following cases:

- Significant heat of solution. The contribution of the heat of solution may even surpass the heat of reaction. Thus an important part of the measured heat is due to solution, and therefore, it is strictly feed-controlled. The MTSR is lowered.

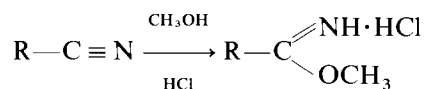
- Side reactions in the temperature interval from the process temperature to MTSR. If a side reaction occurs in this temperature range, its contribution must be taken into account. The MTSR can be higher than the value predicted by the standard method.
- Equilibrium reactions. The conversion of an exothermic equilibrium reaction is thermodynamically limited with increasing temperature. The MTSR may be lowered.
- Presence of unstable intermediates. If unstable intermediates are present their decomposition may strongly affect the thermal stability of the reaction mass and consequently the accumulated potential. The MTSR can be higher than the value predicted by the standard method.
- In many cases the main risk related to the temperature rise to the MTSR is a pressure build-up. This must be integrated into the experimental study of the thermal risks.

The following examples will illustrate some of the cases mentioned above.

## 2. Example 1: synthesis of an imido-ester

### Reaction

An imido-ester is prepared by reaction of a nitrile with methanol and hydrochloric acid



### Process

The nitrile is dissolved in methanol; 185% (mol/mol) of hydrochloric acid gas is then fed over 10 h into the head space of the reactor at 20°C.

#### 2.1. Thermal risks related to this process

##### ● Equipment

Owing to the low reaction temperature and the material of construction (glass-lined steel), the reactor has a limited cooling capacity. Also, because of the complexity of the multipurpose plant, where this reactor is located, a cooling failure cannot be excluded. The reflux condensation system is made of glass and cannot resist a pressure build-up.

##### ● Reaction

The main risk is a loss of control of the desired reaction. There is no high exothermic decomposition reaction. Additionally, due to the evaporation of the solvent and HCl release, a pressure build-up may occur.

A first estimate using a simplified kinetic model gives a critical cooling failure scenario: the temperature will reach the boiling point and the boiling rate will be high enough to produce a pressure build-up which could destroy the glass condenser. This model assumes first-order kinetics, which probably does not correspond to the real reaction mechanism. In order to give a more realistic estimate of the consequences of a cooling failure, more experiments were performed in the reaction calorimeter. The thermal behavior of the reaction mixture between the reaction temperature and the boiling point of the solvent was measured using a temperature ramp after stopping the feed of HCl at different stages of the process. This allows a more accurate estimate of the heat that can be released in the event of a failure. The modified scenario corresponds to a less critical situation.

## 2.2. *Experimental*

The equipment used was the RC1 reaction calorimeter equipped with the standard 2-l glass reactor (AP01) and glass cover. The accessories used were an anchor stirrer, a temperature sensor and calibration heater of 23 W.

As an experimental approach to measure the accumulated heat in the event of a cooling failure, different reaction calorimetry experiments were performed. A first experiment was carried out to determine experimentally the heat of solution of HCl in methanol in the concentration range of the process. Further experiments were then performed to measure the true accumulation of reaction energy. The amount of HCl feed was varied as 25%, 50%, 100% and 185% of stoichiometry. In order to measure the thermal effects in the temperature range between the process temperature and boiling point of the reaction mass, at the end of the feed, the reaction mixture was heated from 20 to 55°C over 35 min and stirred at this temperature for several hours. The heat of reaction measured after the HCl dosing represents the heat which really could be released by the system after a failure in this temperature interval (true accumulated heat).

## 2.3. *Results and discussion*

Fig. 1 represents the results of the reaction calorimetry experiment with 185% HCl feed.

The results of Table 1 show that the boiling point (65°C) cannot be reached, even if the reaction proceeds adiabatically after a cooling/stirring failure. The HCl feed must be stopped immediately after the failure occurs. The feed-controlled exothermic effects are not only due to the heat of solution of HCl in methanol. The measured value of the heat of solution is about 300 kJ/kg HCl in the experiment without nitrile, without the measured heat of reaction. The experiments with nitrile give a value of about 1200 kJ/kg HCl. This value corresponds to additional exothermic reactions, which are partly feed-controlled (for example a protonation which is fast and feed-controlled). In these experiments a significant amount of HCl gas was produced during the heating ramp and this was absorbed in NaOH.

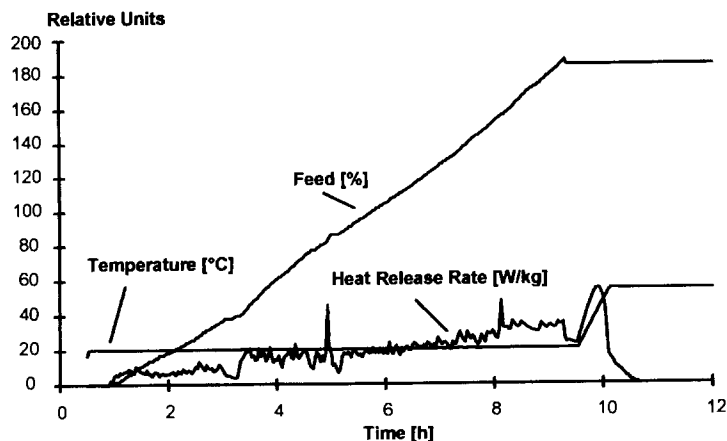


Fig. 1. 185% HCl dosing.

Table 1  
Summary of thermal data obtained in the reaction calorimeter

Experiment	Heat of reaction of the HCl feed/ kJ/kg HCl	Accumulated heat: heating from 20 to 55°C/kJ/kg RM <sup>a</sup>	Adiabatic temperature rise due to the accumulation/°C	MTSR/°C
Methanol + HCl	300	–	–	–
25% HCl	1250	20	10	30
50% HCl	1250	70	35	55
100% HCl	1200	50	25	45
185% HCl	760	60	30	50

<sup>a</sup> RM is reaction mass at the end of the feed.

#### 2.4. Cooling failure scenario

In the case of a cooling/stirring failure, if the HCl dosing is not immediately stopped, a critical situation could be produced: boiling of the reaction mass, HCl desorption and probably a pressure build-up.

If the HCl dosing is immediately stopped after a failure, the experimental measurement of the accumulated heat shows that the temperature can increase by self-heating but the final temperature cannot exceed the boiling point of methanol (65°C). During this self-heating, HCl gas can be produced. This gas should be absorbed in order to prevent its release into the production building. The reaction mass after addition of 185% HCl shows an exothermic decomposition detected at about 80°C. Under worst case assumptions, this could produce an additional self-heating to the boiling point of methanol. In this case a mild boiling could result, which can easily be controlled by activating the condenser with emergency water.

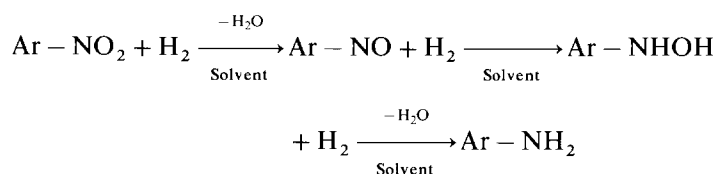
### 2.5. Assessment of the thermal risks

Assuming that the feed can be stopped immediately after the failure (by interlock with temperature for example), self-heating of the reaction mass can only lead to a value slightly below the boiling point of methanol. In the worst case, only mild boiling would be produced.

## 3. Example 2: hydrogenation of aromatic nitro compounds

### Reaction

The hydrogenation of nitro compounds is a very exothermic reaction with several intermediate steps. Unstable phenyl-hydroxylamine sometimes accumulates during the catalytic reaction and may lead to a safety problem [8]



### Process

The stainless-steel reactor is charged with the aromatic compound; solvent and catalyst are added. The mass is maintained at constant temperature during the addition of hydrogen. The pressure is adapted to the heat release.

#### 3.1. Experimental

The following instruments were used to measure the thermal data of the process.

- Reaction calorimeter HP-60 (Mettler) equipped with a 1.8-l stainless steel high-pressure reactor, a fast-running gas dispersion stirrer (1200 rpm) and a thermostated reactor lid. The reactor is designed for a maximum pressure of 60 bar.
- The thermal stability of the reaction mixture was determined by microcalorimetric methods using a Mettler TA 4000. The samples were placed in pressure-resistant (200 bar) gold-plated stainless steel crucibles and analyzed by standard methods (scan rate 4°C min<sup>-1</sup> or isothermal).

#### 3.2. Thermal data of synthesis reaction

The thermal data of the reaction and especially the accumulation of intermediates were determined in the reaction calorimeter. The reactor was charged with the nitro compound, the solvent and the catalyst. The mass was heated to 70°C and maintained at 70°C, 5 bar pressure and a stirrer speed of 1200 rpm. In order to determine if the reaction rate can be influenced by agitation, the stirrer speed was reduced to 400 rpm after 45 min and increased again to 1200 rpm. The effect of possibly accumulated

Table 2  
Results of the reaction calorimeter experiments

Hydrogen uptake	101% of stoichiometry
Heat of reaction	210 kJ kg <sup>-1</sup> or 470 kJ mol <sup>-1</sup>
Heat capacity of reaction mass	2.6 kJ kg <sup>-1</sup> K <sup>-1</sup>
Adiabatic temperature rise	80°C

intermediates was studied in the following way: after 1.5 h the hydrogen was interrupted at a hydrogen uptake stage, where maximum accumulation was expected. The hydrogen atmosphere was replaced by nitrogen. The reaction temperature was increased up to 100°C and later cooled to 70°C. Afterwards the experiment was continued. The thermal data of the reaction are summarized in Table 2 and graphically represented in Fig. 2.

The reduction of the stirrer speed after 45 min (see fig. 2) allows us to stop the heat release; thus the reaction rate can be controlled by the stirrer. No thermal effect was observed during heating. Hence an accumulation of unstable intermediates can be excluded in this case. The maximum attainable temperature (MTSR) is equal to the reaction temperature of 70°C.

The thermal stability of the reaction mass was also studied in a series of DSC experiments. Samples were taken at strategic times during the experiment in the reaction calorimeter and immediately analyzed by DSC (see Figs. 3–5).

The heat of decomposition for the reactants is critical. The energy of decomposition linked to the amount of nitro compound is found at approx. 250°C. During the hydrogenation, the severity progressively decreases. The nitro compound is reduced and the potential of the energy signal of the reaction mass becomes proportionally lower (Fig.4). In this case a weak exothermic signal at approx. 40°C, probably due to an intermediate, can be observed. Triggering all exothermic reactions within the hydrogenation could cause a temperature rise of approx. 60°C. At the end of the reaction, the

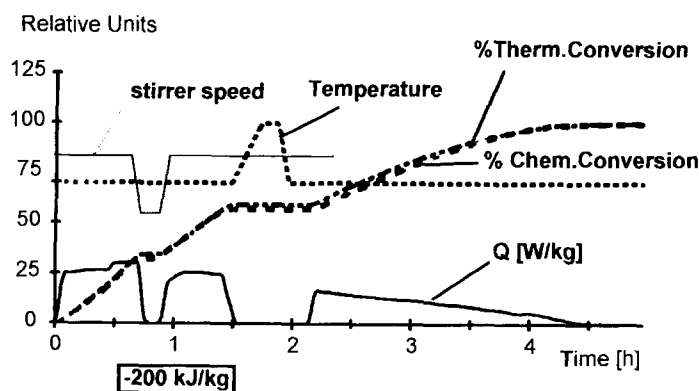


Fig. 2. Hydrogenation of a nitro compound.

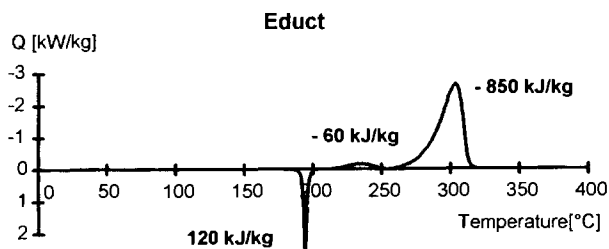


Fig. 3. Reactants mixture before hydrogenation.

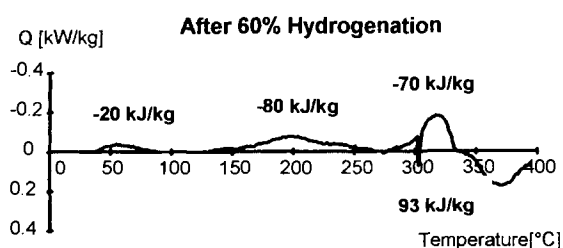


Fig. 4. After 60% hydrogenation.

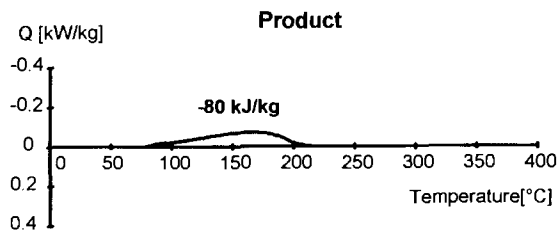


Fig. 5. Final reaction mass.

decomposition peak due to the nitro compound disappears and the severity is assessed to be low. The observed accumulation does not represent any thermal risk.

### 3.3. Analysis of thermal risks

Different failure scenarios were considered:

- Cooling failure: stirrer and hydrogen feed are not stopped  
Starting with a reaction power of  $30 \text{ W kg}^{-1}$  at 5 bar hydrogen pressure and a reaction temperature of  $70^\circ\text{C}$ , the temperature increases to  $150^\circ\text{C}$  within 20 min.



At this point the pressure of the solvent rises also. This scenario could lead to loss of containment and formation of an explosive cloud.

- Cooling failure: hydrogen feed is stopped, agitation is not stopped

The conditions at the instant of the failure are the same as before, but because the hydrogen content of the reactor is limited, the roughly estimated temperature rise is only 10°C. Simultaneously, the pressure decreases from 5 bar to the vapor pressure of the solvent.

- Cooling failure: hydrogen feed and agitation are stopped

In this case the reaction is immediately stopped and no temperature or pressure rise will occur.

- Stirrer failure

The reaction is stopped, thus the temperature and pressure remain stable.

### 3.4. Risk assessment

The desired reaction is well controlled by the hydrogen addition rate, the pressure and the stirring rate. The worst case occurs if after a cooling failure the hydrogen feed is not interrupted and the stirrer not stopped. This results in a hazardous situation with the desired reaction producing a temperature rise of 150°C and corresponding over-pressurization. The first step of the decomposition reaction then raises the temperature to 190°C with a further pressure build-up. The last step of the decomposition however is not triggered within 24 h.

### 3.5. Recommendations

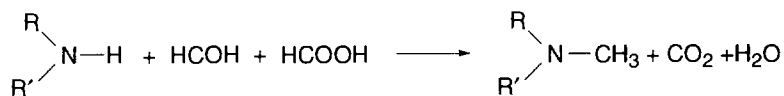
The process is assessed to be safe if the following technical measures can be taken:

- The H<sub>2</sub>-feed rate must be adapted to the heat dissipation rate of the reactor.
- The temperature of the reactor has to be limited by alarm and interruption of the hydrogen feed.
- In case of a cooling failure, the hydrogen supply and agitation has to be stopped immediately. If the temperature or the pressure increases, a *controlled* depressurization must be started. By controlled depressurization, we mean a slow depressurization avoiding two-phase flow. This can be achieved by the slow opening of a control valve.
- The reactor needs pressure control to prevent damaging the reaction vessel. An additional safety valve should be protected by a rupture disc in front of the valve to avoid direct contact of the valve with the reactants (especially solids).
- The reaction temperature and pressure must be kept monitored and in case of an increase in either, the hydrogen feed must be stopped. If a further increase is observed, the pressure must be lowered by *controlled* venting.

#### 4. Example 3: Eschweiler Clark reaction

##### Reaction

A secondary amine is *N*-methylated using an Eschweiler Clark reaction

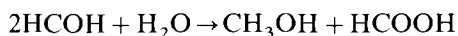


##### Process

The amine is charged together with formaldehyde. Since the amine is a solid the reactor must first be heated up to 80°C without stirring, until the reaction mass is melted. Once the reaction mass can be stirred, the temperature is maintained at 80°C and the reaction started by the addition of formic acid.

##### 4.1. Thermal risks related to the process

During the heating period, before the reaction mass is melted, the temperature control is poor. If a secondary reaction is triggered in this temperature range, it could cause an unwanted temperature and / or pressure increase. It is known, that under these conditions, formaldehyde can give a Cannizzaro reaction



The reaction itself is exothermic but more important is the fact that it produces formic acid, which in turn will allow the main reaction to proceed. For this reason it was decided to study the thermal behavior of the (preloaded) reaction mixture in a reaction calorimeter.

##### 4.2. Experimental

The investigations were performed using a Mettler-Toledo RC1 reaction calorimeter with a 2-l glass reactor equipped with anchor stirrer, glass temperature and calibration probe, pH electrode, distillation kit and gas absorption (NaOH) allowing a mass flow measurement. The evaluation of the experiments was performed using the RC1 evaluation software.

The heat release rate and the heat of reaction were also measured in a Setaram C80 microcalorimeter. The measuring cells were fitted with a pressure-sensitive transducer to follow the pressure change.

The thermal stability of the reaction mass was studied by DSC (Mettler TA 4000) using gold-plated high-pressure crucibles and a scan rate of 4K min<sup>-1</sup>.

##### 4.3. Results and discussion

The DSC experiment shows an exothermic peak with an energy of 300 kJ kg<sup>-1</sup> in the temperature range 85 to 190°C. Thus the energy potential of the reaction mass (without the formic acid) is high. Under isothermal conditions at 80°C, a first step of the reaction with an energy of 160 kJ kg<sup>-1</sup> and an initial heat release rate of approx. 20 W kg<sup>-1</sup> were

measured. The second step was measured by switching again to scanning mode:  $110 \text{ kJ kg}^{-1}$  in the temperature range from 100 to  $210^\circ\text{C}$ . The activation energy of the first step was determined from experiments in the Setaram calorimeter:  $108 \text{ kJ mol}^{-1}$ .

In order to predict the consequences of triggering this reaction, an experiment was performed in the reaction calorimeter. The reaction mass was heated up to  $100^\circ\text{C}$  in  $T_r$ -mode (control of the reactor temperature) and then switched to adiabatic mode. The water evaporated was allowed to distill off and the  $\text{CO}_2$  produced absorbed in caustic soda. The flow rates of vapor and  $\text{CO}_2$  were calculated from the heat of condensation and weight of the absorber respectively. The results are presented in Fig. 6.

The heat of reaction is measured to be  $140 \text{ kJ kg}^{-1}$ . The difference of  $20 \text{ kJ kg}^{-1}$  from the value measured by DSC can be explained by the fact that after switching from temperature control to adiabatic mode, requiring approx. 10 min, the heat flow is undefined owing to heat losses at the reactor lid at the beginning of the distillation. The total amount of  $\text{CO}_2$  corresponds to 90% of theory, the maximum gas flow rate is  $70 \text{ l kg}^{-1} \text{ h}^{-1}$  and the maximum distillate flow rate is  $240 \text{ l kg}^{-1} \text{ h}^{-1}$ . Owing to the evaporation of water, the temperature remains at  $100^\circ\text{C}$ , so that the second step of the reaction is not triggered.

#### 4.4. Cooling failure scenario

From these values, the consequences in the designated plant equipment can be established: in the narrowest part of the equipment, the entrance of the condenser (diameter, 100mm), the vapor and gas velocity will be  $45 \text{ m s}^{-1}$ . At this velocity, flooding will occur [9], which in turn will cause a pressure build-up.

#### 4.5. Assessment of risks

Owing to the bad control of the reaction temperature during the heating period, such a scenario cannot be excluded a priori. The consequence will be an uncontrolled evaporation of water with pressure build-up which could result in the rupture of the glass equipment, vapor tube and condenser.

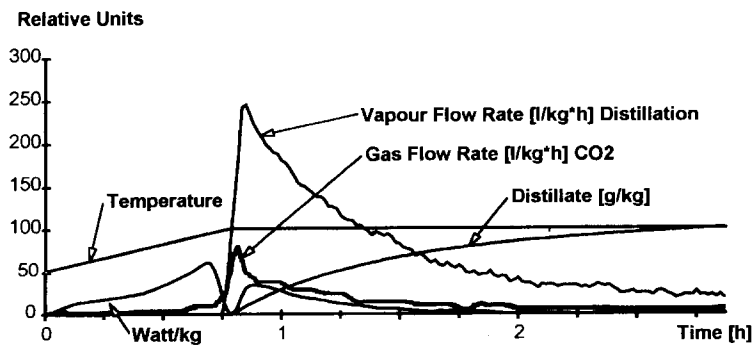


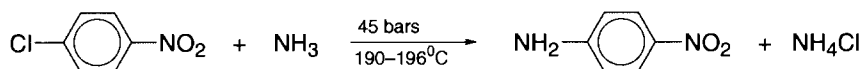
Fig. 6. Results of the reaction calorimetry experiment.

#### 4.6. Recommendations

It was recommended that the process be changed by the use of a solvent to allow good control of the reactor temperature during the heating period and feed of formaldehyde, thus avoiding the high initial energy potential of the reaction mass. In fact this change could be performed without loss of productivity owing to the dilution, because the initial heating period could be shortened.

### 5. Example 4: amination of an aromatic chlorine compound

#### Reaction



#### Process

The process is performed as a typical batch process. The reactor is charged with the chloro-aromatic compound and ammonia (27% in water) at ambient temperature. The autoclave is then heated over 3 h to 195°C and maintained at this temperature for 5 h. The pressure finally reaches 42 bar. After this time the reaction mass is cooled to room temperature.

#### 5.1. Thermal risks related to the process

The risks of a thermal runaway due to an exothermic decomposition reaction are described in detail in many publications [5,6]. Besides triggering a possible decomposition reaction, the pressure build-up caused by uncontrolled heat release of the desired reaction is an important thermal risk especially in industrial synthesis reactions performed under pressure. Therefore in this paper we focus on the consequences of a pressure build-up in the case of a cooling failure. The decomposition of the reaction mass will not be studied here.

#### 5.2. Experimental

The investigations were performed using a Mettler-Toledo RC1 reaction calorimeter fitted with a high-pressure reactor (HP 60, 1.8 l, stainless steel), fast-running stirrer (1100 rpm) and heated cover. The evaluation of the experiments was performed using RC1 evaluation software.

The heat release rate and the potential were also measured in a Setaram C80 microcalorimeter. The measuring cells were fitted with a pressure-sensitive transducer in order to follow the pressure change. A blank was run in the temperature scanning mode to determine the baseline. The same system was used to determine the vapor pressure of the solvent as a function of the temperature.

### 5.3. Results and discussion

To investigate the thermokinetic behavior of the synthesis reaction, experiments were performed in the reaction calorimeter (Fig. 7) and in the microcalorimeter. The results are listed in Table 3. From these measurements the MTSR was calculated for different reaction times. The course of the accumulation and of the MTSR are shown in Fig. 8. In addition, the temperature dependence of the vapor pressure of the solvent was measured in the microcalorimeter (Fig. 9).

### 5.4. Cooling failure scenario

In a worst-case scenario, the cooling failure will occur during the heating period when the reaction mass is about to reach the reaction temperature of 195°C. At this instant, the accumulation is about 65%, leading to a lower MTSR than with the full adiabatic temperature rise of the reaction. Nevertheless at this temperature the heat release rate of the synthesis reaction is  $26 \text{ W kg}^{-1}$ . Without cooling there will be a runaway time of the desired reaction of less than one hour.

In general, one hour is too short for a production process because time is needed to recognize the failure, organize the necessary measures and additional time will pass until the measures become effective. Therefore, the probability is high that within one hour the temperature will rise to 260°C accompanied by an increase of the system pressure up to 100 bar.

### 5.5. Assessment of the thermal risks

The vapor pressure at the reaction temperature is 42 bar, but in the case of a cooling failure the pressure will rise to 100 bar. If the reactor is not built to resist such a pressure, a failure of the cooling system or the stirrer could lead to a dangerous situation.

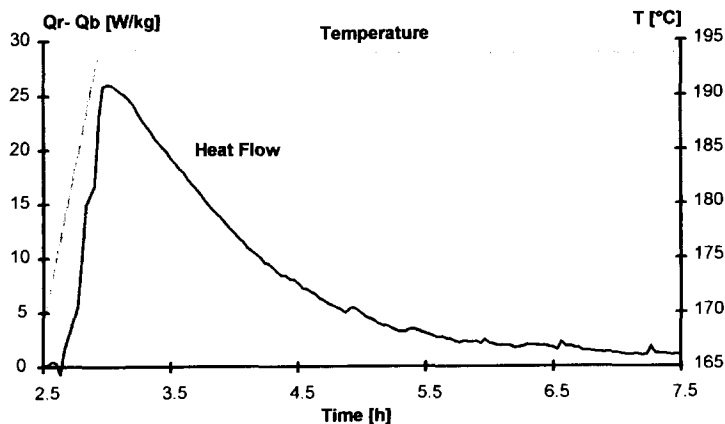


Fig. 7. RC1 experiment. The baseline is drawn manually.

Table 3  
Summary of thermal data of the amination reaction

Exp.	$P_{\max}$ /bar	Stirring rate/rpm	$Q_{\text{realc max}}/\text{W kg}^{-1}$	Heat of reaction/ $\text{kJ/kg FRM}^a$	$C_p/\text{kJ kg}^{-1} \text{K}^{-1}$	$\Delta T_{\text{ad max}}/^\circ\text{C}$
RC1	42	800	26	-210	3.4	62
C80	42	-	16	-215	3.4	63

<sup>a</sup> FRM: final reaction mass.

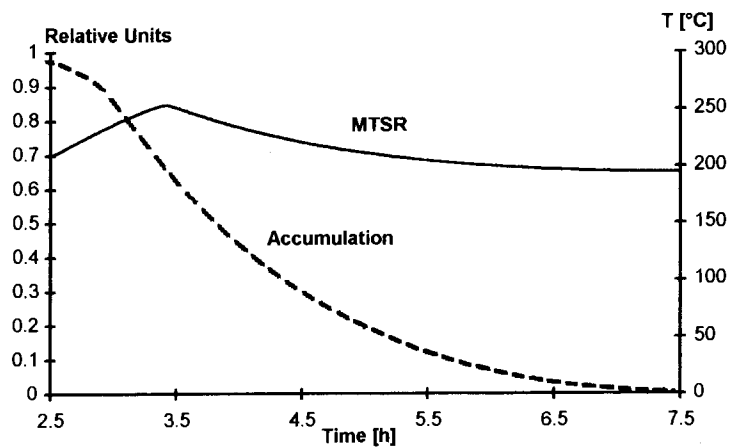


Fig. 8. Calculated accumulation and MTSR.

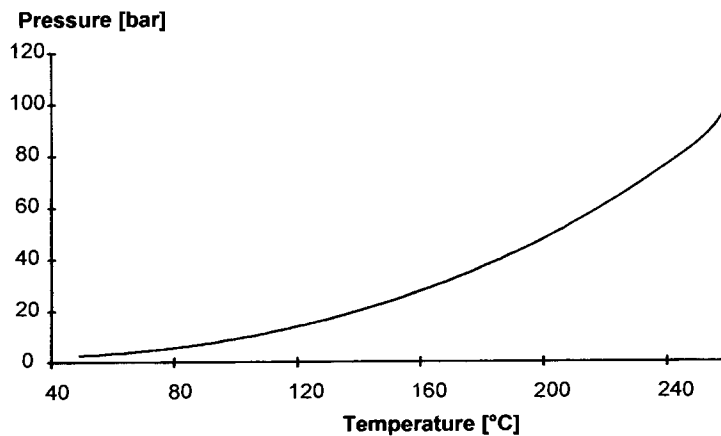


Fig. 9. Vapor pressure of aqueous ammonia (27%).

Suppose the rupture disk or the pressure relief valve opens below 100 bar. The resulting pressure drop would cause vigorous boiling of the overheated solvent. Depending on the characteristics and dimensions of the relief system and the vessel content, flooding of the tube or two-phase discharge will occur. If the relief system is not designed for two-phase venting and containment the consequences could be dramatic:

- discharge of the toxic reaction mass to the environment
- release of explosive vapor
- bursting of the tube and release of a hot vapor and liquid stream
- bursting of the reactor.

### 5.6. Recommendations

Safe plant design for the given process implies an autoclave and a pressure relief system suitable for an overpressure of at least 100 bar. An appropriate system for controlled depressurization composed of a control valve, a condenser and a storage tank behind the condenser can be installed as a last resort.

We recommended that a different synthetic method or a different process be used. In a batch reactor, the course of the reaction can only be controlled by the heat exchange system. In a semi-batch process, the heat release rate and also the accumulation is a function of the feed rate. Therefore by changing the feed rate, the MTSR and the corresponding maximum vapor pressure can be decreased to an appropriate value. Alternatively, a continuous process using a reactor with a small volume and a high heat capacity could be used. This would have the advantage that self-heating of the reaction mixture is not possible owing to the good heat transfer to its mass.

## 6. Conclusions

In order to predict the behavior of a reactor under undesired operating conditions such as a cooling failure, several other factors must be taken into account in addition to purely thermal factors.

- Chemistry, reactivity

Side reactions may take place even with partial charges (as in Example 3) where only the initially charged reactants may lead to a hazardous situations. In semibatch reaction, heats of mixing or solution often provide an important contribution to the overall effects. In such cases (Example 1) the true thermal conversion can only be found after separation of the different contributions.

- Stability of intermediates

During the reaction, if intermediates are formed, the stability of the reaction mass may pass through a minimum. Adequate strategies must be used to assess the behavior of the reactor in such cases (Example 2).

- Pressure effects, boiling, gas release

In some cases, especially when the reaction mass has a significant vapor pressure or when a gas is produced by the reaction, these effects may dominate the purely thermal effects. The experiments must be designed to allow the determination of the required data (Examples 1,2,3,4).

- Controllability of the reaction course

Depending on the severity of a possible failure, external factors must be used to control the reaction course. As an example, if the reaction is diffusion-controlled, the stirrer may be of great use for an easy control of the reaction rate (Example 2). In other cases the feed control may be sufficient. As in all cases, with exothermic reactions the heat exchange system plays a central role in the control of the reaction course. It can also be the key factor for safe process control [10, 11].

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