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PRODUCTION OF MACROCYCLIC LACTONES THROUGH CATALYTIC OXIDATION OF CYCLOHEXANONE

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Abstract

The aim of this work is basically centred in the improvement of the obtention of the peroxides precursors of macrocyclic lactones (C_{11} and C_{16}) through the Story synthesis useful as raw materials for high performance linear polyesters. As a starting point, the yield has been increased respect to the classic synthesis using mild and intrinsically safer reactants. Concretely, a yield of 55% in triperoxide of cyclohexanone has been achieved using 35% hydrogen peroxide and phosphotungstic acid as catalyser. For this intention two factorial experimental designs, fractional and complete, have been carried out. The analytical method adequate for the reactive system studied (HPLC-UV-RI) has been chosen as well as the optimal operating conditions. A quantification of the risk on the first part of the reaction in calorimetric terms has been performed.

Keywords: calorimetry, hydrogen peroxide, macrocyclic lactones, oxidation, reaction safety, Story synthesis

Introduction

Macrocyclic lactones are increased value molecules useful as primers for high performance lineal polyesters, thermoplastic polyurethanes and adhesives, synthetic leather and fabrics, resins for surface coatings, microcellular foams, orthopaedic supports, and stiffeners for shoes, and a lot of different applications with the possibility of making an own design polymer. In particular the thermal or photochemical decomposition of tricyclohexylidene triperoxide yields 16-hexadecanolide (dihydroambrettolide, 16-hexadecanolactone) and cyclopentadecane. 16-hexadecanolide is an important macrocyclic musk lactone with good stability, good odour characteristics and fixative properties to volatile fragrance oils [1–3].

Musks containing macrocyclic structures naturally come from animals or plants and its price has always been very high. Today natural musks have almost completely been replaced by synthetic polycyclic structures, which have become the standard for economic, stable and easy to use musk scent in the perfume, cosmetic, and soap industry. In recent years macrocyclic musks have gained much popularity in comparison to polycyclic musks due to advances in their synthesis and reductions in costs.

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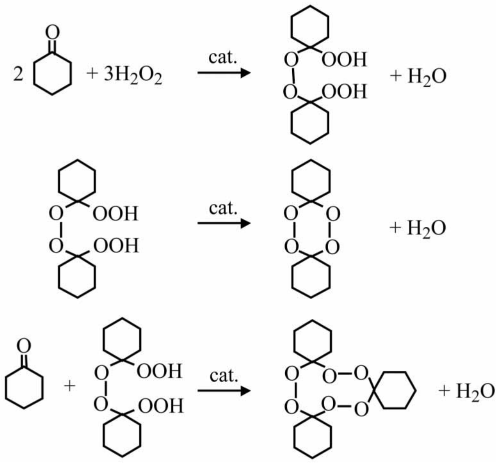
In 1968 Story *et al.* [4, 5] made public a new synthetic method to manufacture macrocyclic musk lactones and ketones. They found out that the decomposition of the appropriate ketone peroxide provides a general and facile synthesis of a large variety of macrocyclic compounds [1, 3].

The successful application of this method depends in particular upon the synthesis of the desired peroxide. Tricyclohexylidene triperoxide, the precursor for the synthesis of 16-hexadecanolide, can be obtained by a catalytic oxidation of cyclohexanone with hydrogen peroxide [4], a reaction which has subsequently been improved and modified along time [6–8]. Even in the limited area of methods in which the triperoxide was obtained in a single step from cyclohexanone and hydrogen peroxide, several peroxide products may be obtained by only a slight change in reaction conditions, which complicates the optimisation of this reaction (Scheme 1).



Scheme 1 Scheme of Story synthesis reaction

The synthesis of macrocyclic lactones, proposed by Story consists of two steps:

1. Catalytic oxidation of cyclohexanone with hydrogen peroxide to obtain macrocyclic peroxides.
2. Thermal or photochemical decomposition of the obtained peroxides to yield macrocyclic lactones.

Despite the obvious hazardous nature of the preparation and decomposition of the cyclohexanone triperoxide, this general method of preparing 16-hexadecanolide, now known as the Story synthesis, presents a very economical approach to macrocyclic lactones. Our group proposes a modification of the mentioned synthesis [4, 5] providing a possible application of this process in industrial scale. This work focuses on the synthesis of tricyclohexilidene triperoxide by a catalytic oxidation of cyclohexanone with hydrogen peroxide in 35% concentration. The so far preferred hazardous catalyst perchloric acid ($HClO_4$) has been replaced by a more safely manageable substance, the phosphotungstic acid hydrate. Moreover, the hydrogen peroxide concentration has been reduced to 35% in comparison to 90% proposed by Story. The reaction conditions have been optimised concerning reaction temperature, reaction time, molar relation of the reactants and amount of catalyst.

The reaction of cyclohexanone with hydrogen peroxide, even at only 35%, is extremely exothermic. The possibility of hydrogen peroxide to decompose into oxygen and water, as well as possible decomposition reactions of the obtained products, implies an obvious hazardous nature of the reaction. The objective of this work is to develop a safety study of the process considering all possible accident scenarios during the evolution of the reaction. Also the safety measure of a quenching with water in case of coolant failure is studied.

Experimental section

Reaction

Table 1 shows the chemicals, which have been used in the experiments. The reaction has been carried out isothermally at 70ºC. The temperature was controlled by means of a thermostat (Julabo VC 12B). A solution of phosphotungstic acid hydrate and cyclohexanone has been prepared at room temperature and then heated up to process temperature. Then, hydrogen peroxide 35% was added. The mixture was stirred by a magnetic stirrer (P Selecta Agimatic-E) at approximately 900 rpm.

Table 1 Reactants used for all performed reactions

Substances	Manufacturer	Reference
Cyclohexanone	Fluka	29150
Phosphotungstic acid hydrate	Panreac	121033
Hydrogen peroxide, 35%	Fluka	95299

Reactions corresponding to the experimental design have been performed in test-tubes with a total reaction volume of approximately 1.3 mL. At the desired reaction time one tube was removed from the bath and cooled down to ambient temperature ready to proceed with HPLC analysis.

The safety study reactions have been carried out in the reaction calorimeter RC1® of Mettler-Toledo with the AP01 2 L glass reactor. Glass anchor stirrer with speed set at 200 rpm, the Mettler MT01 thermostatic cover, a reflux condenser, an electrical calibration heater, sensors for reaction temperature (T_r), jacket temperature (T_j), lid temperature (T_{lid}), inlet and outlet water temperature of the condenser $T_{c,in}$ and $T_{c,out}$, dosing pump (Prominent Gugal G4a0308TT1000A0000) with balance (Mettler PM6100), and the necessary connections. The temperature of the isothermal reaction has been set to 70°C.

Method

The product and reactants concentration evolution was determined by High Performance Liquid Chromatography (HPLC). The complete contents of each test tube was used as a sample and diluted in the mobile phase of the chromatograph at 1% (mass). The mobile phase used was a mixture of acetonitrile (Fluka 00687) and micro filtered water in a volumetric relation of 75:25. The flow of the mobile phase in the column was 1 mL min^{-1}.

The equipment is a liquid chromatograph of Hewlett Packard series 1050. The samples are analysed by ultraviolet detector (UV) at 254 nm wavelength, and thermostatic refractive index at 30°C. The used separation column was a Merck RP18.

Theoretical background

The Reaction calorimeter RC1® of Mettler-Toledo uses the method of heat flow calorimetry. The basic equation of this type of reaction calorimetry is the heat balance of a stirred tank reactor:

$$m_\mathrm{r} c_\mathrm{pr} \frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}t} = UA(T_\mathrm{j} - T_\mathrm{r}) + \dot{Q}_\mathrm{r} + \dot{Q}_\mathrm{loss} + \dot{Q}_\mathrm{dos} + P_\mathrm{stirrer} + P_\mathrm{heater} \tag{1}$$

with U – global heat transfer coefficient, A – heat transfer area, $\dot{Q}_\mathrm{r}$ – exothermic power of the chemical reaction, $\dot{Q}_\mathrm{loss}$ – power of heat loss to environment (negative), $\dot{Q}_\mathrm{dos}$ – power of heat absorption/release by dosed substances, P_stirrer – power of the stirrer, P_heater – power of the electrical (calibration) heater.

The specific heat of the reaction mixture c_pr and the global heat transfer coefficient U are determined by calibrations before and after the reaction. An interpolation is carried out between these values, whose exact conditions are defined by the user. The power input of the stirrer P_stirrer is obtained by measuring the torque of the stirrer shaft. The heat loss $\dot{Q}_\mathrm{loss}$ of the reactor is usually determined by calibrations, but the use of a thermostatic lid accomplishes that it can be neglected in our case. In case of dosing or removal of material to or from the reactor a convective term must be considered:

$$\dot{Q}_\mathrm{dos} = m_\mathrm{d} c_\mathrm{pd} (T_\mathrm{d} - T_\mathrm{r}) \tag{2}$$

with T_d – temperature of the dosed substance.

Reaction calorimetry is a very suitable device to characterise thermally a chemical process. In this work it was used to determine the necessary parameters of the catalytic oxidation of cyclohexanone with hydrogen peroxide. These are the heat of reaction in a semi-batch process and the gas evolution. With this information the necessary cooling and gas removal capacities of the reactor can be determined. In addition the acquired data is used to estimate the danger related to the desired reaction. Last but no least the reaction calorimeter offers the possibility to simulate a cooling failure by operating the reactor in adiabatic mode. In this work the RC1® was used to simulate a cooling failure and a quenching of the reaction mass.

A good indicator of the process inherent safety is the *MTSR*. The maximum temperature attainable by the synthesis reaction is the temperature that will be reached when an exothermic primary reaction is left under adiabatic conditions. The temperature rise from the process temperature to the *MTSR* is called 'adiabatic temperature increase ΔT_{ad}'.

$$MTSR = T_{\mathrm{P}}+\Delta T_{\mathrm{ad}} \tag{3}$$

If an exothermic reaction is kept under adiabatic conditions, the entire reaction enthalpy is converted into a temperature increase of the reaction mixture. If the heat accumulation by the reactor itself is omitted, T_{ad} can simply be calculated by dividing the reaction enthalpy by the heat capacity of the system:

$$\Delta T_{\mathrm{ad}} = \frac{\Delta H_{\mathrm{r}}}{mc_{\mathrm{P}}} \tag{4}$$

There are different scenarios to be considered when calculating the *MTSR* of a process [9].

Batch scenario

If the addition of the remaining reactant is instantaneous at the moment that adiabatic conditions are reached (t_{ad}), the resulting scenario is called batch scenario. The adiabatic temperature increase is calculated as a function of time by

$$\Delta T_{\mathrm{ad}}^{\mathrm{batch}} = \frac{\int_0^{\mathrm{t}} \dot{Q}_{\mathrm{r}}(t)\mathrm{d}t - \int_0^{\mathrm{t_{ad}}} \dot{Q}_{\mathrm{r}}(t)\mathrm{d}t}{(m_{\mathrm{r}} c_{\mathrm{pr}})_{\mathrm{f}}} \tag{5}$$

with *f* – final conditions.

The maximum value is obtained at the beginning of the reaction when the whole reaction mass will still react. Its value is calculated by

$$\Delta T_{\mathrm{ad}}^{\mathrm{batch,\ max}} = \frac{\int_0^{\mathrm{f}} \dot{Q}_{\mathrm{r}}(t)\mathrm{d}t}{(m_{\mathrm{r}} c_{\mathrm{pr}})_{\mathrm{f}}} \tag{6}$$

It has to be noted that, because the addition is supposed to be instantaneous, the heat capacity of the reaction mass is taken to be equal to the heat capacity of the final mixture.

Stop scenario

In the stop scenario dosing is stopped instantaneously when adiabatic conditions are reached, so the heat capacity can be considered the one in that precise moment. The adiabatic temperature increase as a function of time is proposed to be calculated by

$$\Delta T_{\mathrm{ad}}^{\mathrm{stop}}=\frac{\tau\int_{0}^{\mathrm{f}}\dot{Q}_{\mathrm{r}}(t)\mathrm{d}t-\int_{0}^{\mathrm{t_{ad}}}\dot{Q}_{\mathrm{r}}(t)\mathrm{d}t}{(m_{\mathrm{r}}c_{\mathrm{pr}})_{\mathrm{t_{ad}}}} \tag{7}$$

with τ being a dimensionless reaction time according to

$$\tau=\frac{t}{t_{\mathrm{stoich\,dosing}}}\quad \text{for } t<t_{\mathrm{stoich\ dosing}} \quad \text{and} \quad \tau=1 \quad \text{for } t\geq t_{\mathrm{stoich\ dosing}}$$

Non-stop scenario

This scenario results when dosing is not stopped after adiabatic conditions are reached, the heat capacity is calculated as a mean of the actual and final one. The equation proposed for this case is

$$\Delta T_{\mathrm{ad}}^{\text{non-stop}}=\frac{\int_{0}^{\mathrm{f}}\dot{Q}_{\mathrm{r}}(t)\mathrm{d}t-\int_{0}^{\mathrm{t_{ad}}}\dot{Q}_{\mathrm{r}}(t)\mathrm{d}t}{\frac{(m_{\mathrm{r}}c_{\mathrm{pr}})_{\mathrm{t_{ad}}}+(m_{\mathrm{r}}c_{\mathrm{pr}})_{\mathrm{f}}}{2}} \tag{8}$$

Results and discussion

The fractional experimental design carried out in order to obtain the best yield of triperoxide of cyclohexanone was 2^{4-1}. Each of the four factors was set between two levels. These factors were temperature, reaction time, amount of catalyser and molar relation between cyclohexanone and hydrogen peroxide. In Table 2 all the experiments with the initial corresponding experimental conditions are shown. The response of each experiment is given in triperoxide yield and cyclohexanone conversion, calculated from the concentration determined by HPLC analysis of the final reaction mass.

From the ANOVA analysis of the response obtained whom may realise that factors *B* (amount of catalyser) and *C* (hydrogen peroxide proportion) are significantly different from 0 with a 95% certainty.

The following factors in significance are the interaction *BD* (confused with the interaction *AC*) and factor *D*. The optimal conditions of reaction are extracted from further experimental design based on the first one. More details of these conditions are not given for confidentiality reasons. The safety study has been performed working in these optimal conditions for future considerations in the scale-up of the process.

Thus, the catalytic oxidation of cyclohexanone with hydrogen peroxide 35% has been carried out in semi-batch mode in the reaction calorimeter RC1®. The reaction temperature was 70ºC and the dosing of H_2O_2 was completed in 30 min, reaching a rate of dosing of 1.87 L h^{-1}. The reaction has been left at isothermal conditions for 21.5 h.

Table 2 Experimental conditions and yields obtained for initial experimental design

Exp.	Code	Factors				Real factors				Response	
		A	*B*	*C*	*D*	*T*/°C	g cat/g cyc	cyc/per	*t*/h	conv. cyc	Trip yield
1	(1)	–1	–1	–1	–1	65	0.01	1.11	1	82.84	22.55
2	a(d)	1	–1	–1	1	75	0.01	1.11	2	80.83	22.15
3	b(d)	–1	1	–1	1	65	0.03	1.11	2	79.06	35.64
4	ab	1	1	–1	–1	75	0.03	1.11	1	82.88	22.75
5	c(d)	–1	–1	1	1	65	0.01	0.66	2	83.32	11.75
6	ac	1	–1	1	–1	75	0.01	0.66	1	89.26	12.73
7	bc	–1	1	1	–1	65	0.03	0.66	1	81.23	21.57
8	abc(d)	1	1	1	1	75	0.03	0.66	2	90.34	28.54

Reaction at 70°C

With the experiment carried out in the Reaction calorimeter the power of heat generation for a period of 21.5 h was obtained. As it can be seen in Fig. 1, very strong exothermic activity is detected, as soon as dosing of hydrogen peroxide 35% is initiated. The maximum power is reached after 11 min of dosing and has a value of 578 W corresponding to 525.1 W kg^{-1} if the reaction mass present in that moment is considered. At this time the maximum temperature difference between reaction and jacket temperature is reached and is 56.7°C.

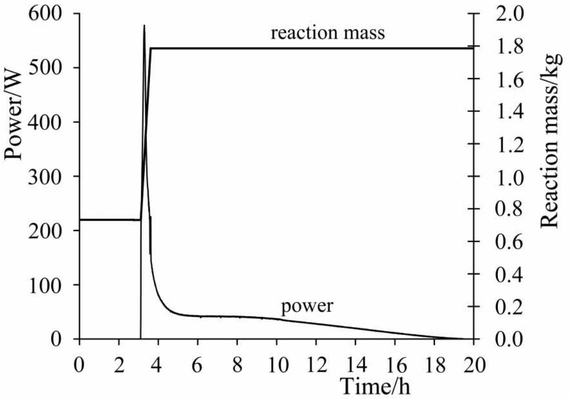


Fig. 1 Power profile of the reaction performed in the RC1

At the end of dosing (30 min of reaction) the power has reached a value of 225 W corresponding to 90 W kg^{-1}. It diminishes to a value of approximately 44.6 W (25 W kg^{-1}) after 2 h of reaction, and a very long exothermic activity (>14 h) is detected from here on.

Obviously the first peak refers to the desired reaction between cyclohexanone and hydrogen peroxide forming the tricyclohexilidene triperoxide and by-products. The reaction occurs thermally very fast and has come near to its end at the end of dosing. It is assumed that the following exothermal activity detected in the RC1® refers to consecutive reactions as well as to the decomposition of the hydrogen peroxide, triperoxide of cyclohexanone and by-products (e.g. dicyclohexilidene diperoxide).

With the obtained power over time the total energy of reaction was calculated by integration. The value obtained for the total exothermic activity is 1285 J g^{-1}. Energy values of more than 500–700 J g^{-1} are considered to be of the order of explosives and thus have to be treated with extreme care [10]. The gas evolution has been measured during the process. Although there was much noise in the obtained signal, the total amount as well as the maximum gas evolution rate has been determined. The total amount of gas evolution during the whole process of dosing (30 min) is $8.7\cdot10^{-3}$ L per gram dosed H_2O_2. During reaction the maximum gas evolution rate is $9.2\cdot10^{-4}$ L per gram dosed H_2O_2, overlapping in time with the power peak. The shape of the curve is quite similar to the shape of the power of the reaction. Two different effects lead to this: First, the rise of the temperature, which could not entirely be suppressed by the thermostat of the RC1®, leads to an expansion of the gas and therefore to an increasing gas flow. The maximum temperature of the reaction was 77.3°C and was reached after 11.5 min of reaction. Secondly the decomposition of hydrogen peroxide releases oxygen, which is detected during the reaction and the following decompositions, and also increases with temperature.

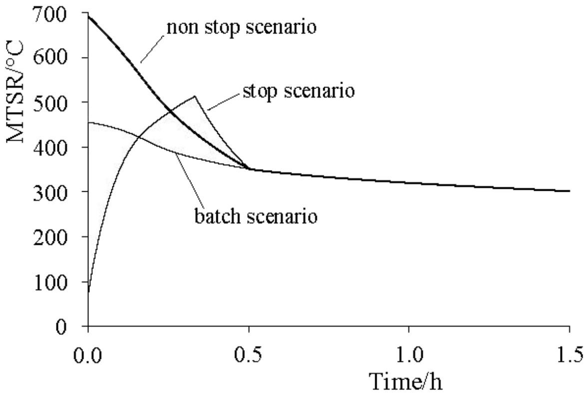


Fig. 2 *MTSR* of the main reaction for different reaction accident scenarios. Batch scenario, stop scenario and non-stop scenario

Moreover, it has to be remarked, that the magnitude of the gas flow is at the lower limit of detection of the flow-meter, whose range goes from 0 to 15 L h^{-1}.

It is concluded, that at least part of the decompositions, probably not all, take part at process temperature and dominate the process thermally at long reaction times (t_r>2 h). This overlap of reaction and decompositions requires the calculation of the *MTSR* considering not only the energy of the primary reaction, but also the part of the decomposition, which takes place at process temperature. The *MTSR* of the process was calculated according to the three scenarios introduced before (theoretical section). The *MTSR* as a function of reaction time is shown in Fig. 2. The maximum values are

$$MTSR_{\mathrm{batch}} = 455.2°\mathrm{C} \tag{9}$$

$$MTSR_{\mathrm{stop}} = 512.8°\mathrm{C} \tag{10}$$

$$MTSR_{\mathrm{non\text{-}stop}} = 690.9°\mathrm{C} \tag{11}$$

These calculations are based on certain assumptions concerning the specific heat capacity. During the reaction the specific heat capacity c_p changes from an initial value of 1961 J (kg K)$^{-1}$ before dosing to 3335 J (kg K)$^{-1}$ at the end of the experiment. In the evaluation this change has been assumed to take place only during dosing, because the water in the dosed hydrogen peroxide 35% rises the c_p significantly due to its own high heat capacity of 4180 J (kg K)$^{-1}$. All possible further change of c_p during the reaction is not considered.

The non-stop scenario results in the highest value, which will be reached in case of a cooling failure at the beginning of dosing. From this the following conclusion is drawn: In the design of the process it has to be assured by all means, that this scenario can never occur. This means, that a secure shut-off of the supply line in case of a failure of the cooling system has to be assured. In the same way, the dosing should be stopped safely in case of an error in the agitation of the system, because good agitation is necessary for the heat transfer to the jacket and to avoid accumulation. If this is assured the non-stop scenario does not need to be considered in the safety study.

The higher value of the stop scenario respectively to the batch operation is due to the lower resulting heat capacity in case of stopped dosing. The maximum value is reached during dosing in the point of stoichiometric relation of cyclohexanone and hydrogen peroxide. From this it could be concluded that once the stoichiometric amount of H_2O_2 has been dosed, it might be better to keep dosing in case of a failure of the cooling system in order to increase the heat capacity of the system. However, it is much more reasonable to add pure water instead of more H_2O_2 in order to increase the heat capacity and absorb the produced heat. This measure is called quenching and will be discussed in the following section. All obtained values show a great danger potential of the process. Not only that the values are extremely high, also the time in which they are reached is short due to the power of the reaction.

Experimental simulation of a cooling failure

The evaluation of the normal process has shown that a failure of the cooling system would increase the process temperature in a way that the process would end in a runaway, if no safety measures are taken. For this reason it is suggested to use the protective safety measure of quenching in case of an accident to control the reaction. This means that in the instant that an error in the cooling system or of the stirring is detected, readily available water at a low temperature will automatically be dumped into the reactor vessel to re-establish temperature control over the system. The measure of quenching has three different impacts on the reaction mass. These are

- cooling of the reaction mass → diminish gas evolution and slow down kinetics of the reaction (Arrhenius factor)
- dilution of the reaction → slow down kinetics of reaction (concentration factor)
- absorption of heat by dosed liquid.

In order to demonstrate the effectiveness of a quenching, experimental validation is necessary (Fig. 3). To simulate experimentally the cooling failure, the reaction was performed as before until the end of dosing. At this point the calorimeter was set in adiabatic mode to emulate an error in the cooling system. Seven minutes after setting the adiabatic mode, 600 mL of water with a temperature 5°C have been added instantaneously to the reactor, which had a fill of 1304 mL. When the quenching is carried out, the temperature drops instantaneously by 22ºC, from 78 to 56°C. In the following 110 min the reaction temperature rises again up to a temperature of 99.4°C and a maximum gradient of 1.85 K min^{-1}. At this time the cooling system was

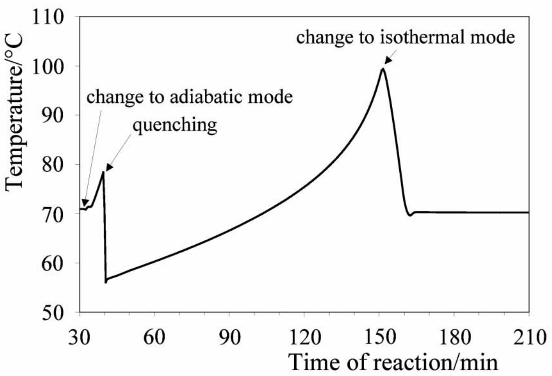


Fig. 3 Temperature evolution in quenching experiment

re-established in order to re-achieve temperature control over the system. The reaction mass has been cooled down to the original reaction temperature of 70°C.

The most important observation to be concluded from the experiment is the fact, that the reaction is not 'killed' by the amount of water used for the quenching. This means, that quenching cannot be a safety measure alone. It might be applied to gain time, but has to be accompanied by other measures. After a quenching, the temperature control of the reaction has to be re-established somehow. It is recommendable to use a significantly larger amount of water for the quenching than in this experiment, or, even better, to dump the whole reaction mass into a large vessel with sufficient cold water.

The best way to assure a safe conduction of this reaction would be to change reaction conditions. However, the process has been optimised for good yield and the complexity and sensitiveness of the reaction make it very hard to find other conditions with equal efficiency. Consequently, another way is intended to be found. Knowing and being aware of the dangerous potential of the reaction, its safe conduction can be achieved by employing especially reliable equipment and implementing preventive and protective safety measures [11].

Conclusions

In the reaction at 70°C the highest value of *MTSR* is obtained by the application of the non-stop scenario. In case that the exclusion of this scenario can be assured by safety measures, the value to consider is *MTSR* = 512.8°C, obtained with the stop scenario. This value signifies that a runaway of the primary reaction is crucial and has to be avoided with help of the design of the process (safety measures).

A cooling failure and subsequent quenching of the reaction mass with water has shown, that the reaction can be slowed down significantly, and can be controlled in case of this accident. Very quick action is necessary after detection of the error in the cooling system (not more than some minutes). In order to gain sufficient time the quenching has to be done by doubling at least the reaction mass (depending on temperature of quench water).

Considering the behaviour of the reaction and the calculated numbers, it has to be concluded that extreme care is necessary to carry out this reaction safely. Surely, a batch-reaction in a large scale is not safely possible. Knowing the dangerous potential and being aware of it, a reaction is semi-batch mode and with a very low rate of addition might be possible, if highly reliable safety measures can assured.

In consequence, the time to take further actions after a quenching in the tested conditions will be of at least 110 min. In this time, temperature control of the reaction mass has to be re-established in some manner and the reaction has to be observed for several hours, since the induction time will be longer with lower temperature and more dilution.

In order to apply the reaction in industrial scale it is recommended to change the process to a continuous reactor. The general disposition could be formed of a PFR reactor, with good heat exchange capability, and a CSTR attached after for the exhausting of the reaction.

Nomenclature

A/m^2	heat transfer area
c_{pd}/J (kg K)$^{-1}$	specific heat of dosed substance
c_{pr}/J (kg K)$^{-1}$	specific heat of reaction mixture
ΔH_r/kJ kg^{-1}	heat of reaction
m/kg	mass
M/g mol^{-1}	molar mass
m_r/kg	mass of reaction mixture
m_d/kg	dosed mass flow
$MTSR$/°C	maximum temperature attainable by runaway of synthesis reaction
n/mol	number of moles
P_{heater}/W	power of the heater
$P_{stirrer}$/W	power of the stirrer
$\dot{q}_r$/W kg^{-1}	specific power of the reaction
$\dot{q}_{r\,max}$/W kg^{-1}	maximum specific power of the reaction at specific isothermal temperature
$\dot{Q}_r$/W	power of reaction
Q_{loss}/W	heat loss to the environment
Q_{dos}/W	heat release/absorption of the dosed substances
$T_{initial}$/°C	initial temperature: temperature in DSC, at which the power signal leaves the baseline
T_d/°C	dosing temperature
T_j/°C	Jacket temperature
T_p/°C	process temperature
T_r/°C	reaction temperature
ΔT_{ad}/K	adiabatic temperature increase
U/W m^{-2} K^{-1}	global heat transfer coefficient

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