Hazard Assessment of and Recommendations for an Organic Peroxide Synthesis

vorgelegt von

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Wer kämpft, kann verlieren.

Wer nicht kämpft,

hat schon verloren.

(Bert Brecht)

Für David

Vorwort

Die vorliegende Arbeit entstand während meiner Tätigkeit als wissenschaftliche Mitarbeiterin am Fachgebiet Anlagen- und Sicherheitstechnik der TU-Berlin.Während dieser fünf Jahre haben etliche Menschen dazu begetragen, dass ich diese Arbeit erfolgreich beenden konnte. Es sei daher an dieser Stelle allen Helfern gedankt!

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Abstract

PEUKERT, Tanja:

Gefahrenbeurteilung und Empfehlungen für eine organischen Peroxidsynthese

Reaktionen mit Peroxiden stellen häufig ein Sicherheitsrisiko dar, da sie durch ihre spezielle O-O Bindung meist thermisch instabil sind. Dennoch werden sie vielfach in der Polymerchemie eingesetzt.

Die Beurteilung der potentiellen Gefahren eines Stoffes oder Prozesses wird in Deutschland meist anhand der Schemata der Technischen Regel TRAS 410 durchgeführt. Nach der Analyse aller am Prozess beteiligten Reinsubstanzen wird der Prozess selbst untersucht bevor mögliche Prozessabweichungen und ihre Folgen analysiert werden. Nach diesen Untersuchungen kann in der Regel eine sichere Prozessfahrweise empfohlen werden.

In der vorliegenden Arbeit wurde die Synthese eines Di-Peroxides aus einem Feststoff und einem Hydroperoxid untersucht. Diese Untersuchungen waren nicht nur aufgrund der Heterogenität des Systems, aus einem fest-flüssig-flüssig wurde im Laufe der Reaktion ein flüssig-flüssig Gemisch, problematisch, sondern auch aufgrund des hohen thermischen Potentials der Reaktion. Ferner konnte in Untersuchungen festgestellt werden, dass neben der eigentlichen Synthesereaktion parallel eine Zersetzung des Hydroperoxids stattfindet. Dies führte dazu, dass ein Simultanreaktions-System untersucht werden musste: die Synthesereaktion, bestehend aus zwei Folgereaktionen, und parallel dazu die Zersetzungsreaktion.

Eine Bestimmung reaktionskinetischer Kenndaten eines Parallelreaktionssystems ist oft schwierig bis unmöglich. Für das vorliegenden System konnte jedoch gezeigt werden, dass sich mit Hilfe von Rücksimulationen einiger Experimente in einem Reaktionskalorimeter, reaktionskinetische Parameter ermitteln lassen, die das System gut beschreiben. Für den 1l-Massstab konnte daher mit Hilfe der anhand der TRAS 410 ermittelten Parameter eine Prozessempfehlung gegeben werden.

Abstract

PEUKERT, Tanja:

Hazard Assessment of and Recommendations for an Organic Peroxide Synthesis

Organic peroxides are, due to their weak O-O-bond, very reactive substances and usually require special attention from the aspects of process safety. Nevertheless they are often used in the polymer chemistry.

In Germany the hazard assessment of substances as well as processes often follows the schemes in the German Technical Regulation TRAS 410. Following these schemes, first all substances have to be analysed in their pure form, then the analysis of the process follows and finally possible process deviations are analysed. Having performed the required analyses, usually a recommendation for a safe process can be given.

In this work the production of a di-peroxide out of a hydroperoxide and a solid was analysed. Problems were not only caused by the heterogeneity of the system, which changes during the reaction from a solid-liquid-liquid to a liquid-liquid system, but also by its high exothermal enthalpy. During the analysis of the process it was furthermore detected that the system consists of three simultaneous reactions. The di-peroxide is produced within two consecutive reactions and parallel there is a decomposition reaction of the hydroperoxide.

The determination of kinetic parameters of a simultaneous reaction system is often difficult. Although, in this work it could be shown that with the help of re-simulations of experiments in a reaction calorimeter, kinetic parameters for the three side reactions can be determined. With the help of these kinetic parameters and the analysis according to the TRAS 410, recommendations on a safe process in a 1l-scale could be given.

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Symbols and frequently used abbreviations

Symbol	dimension	signification
A	m^2	mass transfer area, heat transfer area
BR	-	batch reactor
c	mole/l	concentration
c_p	J/(g·K)	specific heat capacity
CSTR	-	continuously stirred tank reactor
D	m^2/s	diffusion coefficient
Da	-	Damkoehler number
DSC	-	differential scanning calorimetry
E	J/mole	activation energy
HR	K/min	heating rate
k	$(l/mole)^{n-1} \cdot s^{-1}$	rate constant
k_i	m/s	mass transfer coefficient
k_w	$J/(m^2 \cdot s)$	overall heat transfer coefficient
k_∞	$(l/mole)^{n-1} \cdot s^{-1}$	pre-exponential factor
m	kg	mass
n	mole	number of moles, reaction order
$\dot{q}$	W/g	specific heat output rate
$\dot{Q}$	W	heat output rate
Q	J	thermal energy
r, r(T)	mole/(l·s)	rate of reaction
R	J/(mole·K)	universal gas constant

R^2	-	coefficient of determination
SBR	-	semi batch reactor
St	-	Stanton number
t	s	time
T	K	temperature
TEVT	-	thermal explosion vessel test
TMR	s	time to maximum rate
TS^U	-	thermal screening unit
U	$W/(K \cdot m^2)$	heat transfer coefficient
V	l	volume
X	-	conversion

greek symbol	**dimension**	**signification**
α	W/K	heat transfer coefficient
δ	m	thickness (of the film)
$\Delta_R H$	J	enthalpy
$\Delta_R h$	J/mole	specific enthalpy
ΔT_{ad}	K	adiabatic temperature rise
ε	-	volume increase factor
λ	-	stoichiometric input ratio
ρ	kg/m^3	density
Φ	-	thermal inertia
$\Phi(X)$	-	dimensionless reaction rate
ν_i	-	stoichiometric coefficient
ξ_i	-	extent of reaction for reaction i

abbreviation/indices	signification
0	initial or reference state
accu	accumulation
add	addition
chem	chemical
c	cooling
cat	catalyst
char	characteristic
dec	decomposition
di-p	di-peroxide
env	environment
hp	hydroperoxide
im, IM	intermediate
iso	isothermal
j	jacket
k	component
max	maximal
min	minimal
R, r	reaction
sim	simulated
therm	thermal
w	wall

Chapter 1:

Introduction

Due to great and hazardous accidents like for example the release of more than 40tons of methylisocyanate in Bhopal, India, 1984 and of dioxin in Seveso, Italy, 1976 the safety technology got more and more importance for the chemical industry. The implementation of new processes in large reactors requires now a broad safety assessment. For normal chemical processes, which means homogeneous systems with a single reaction, safety criteria have been developed which can be applied in order to ensure a safe process. In Germany for example there is a technical rule called TRAS 410, which can be applied for homogeneous liquid-liquid reactions in order to ensure a safe process. For heterogeneous systems up to now no corresponding technical regulation exists.

Further, the risk of an accident is always strongly related to the characteristics of the chemicals handled. Among the substances with the highest hazard potential are the organic peroxides. Organic peroxides are widely used in the chemical industry, mostly (to approximately 90%) in the plastics industry as an initiator for polymerisation. Their great hazard potential is due to their usually highly exothermic decomposition, which for some peroxides already start at room temperature.

In this work an unknown heterogeneous peroxide synthesis was analysed. This peroxide synthesis is of interest to an industrial partner and is planned to be operated on an industrial scale. It is not only a heterogeneous, but also a highly exothermic reaction. As overall safety criteria for heterogeneous systems until now do not exist, a way had to be found to analyse this heterogeneous process and then give recommendations on a safe handling of it.

As already mentioned, a common method for analysing a newly developed, homogeneous process is described in the German regulation TRAS 410. Although this technical regulation is originally only meant for homogeneous reactions, it was applied to the heterogene-

ous organic peroxide synthesis. The TRAS system was used because of its underlying methodology, which should be generally applicable, and it would be good to amend it with details for heterogeneous systems as well. A first attempt was therefore undertaken with the analysed heterogeneous peroxide synthesis.

Another aim of this work is the safe scale up of this heterogeneous organic peroxide synthesis from laboratory to industrial scale. The difficulties of a scale-up result from the different ratio of the cooling jacket area to the volume of the reactor and of different mixing conditions and in consequence the necessary adaption of feed times between laboratory and plant scale. As the jacket of a chemical reactor is cooled to remove the released heat of the reaction and keep the reaction stable, the area of the heat transfer is an important parameter for the cooling efficiency of the process. While the area of the cooling jacket is still large with respect to the reactor volume for a laboratory reactor, the ratio area/volume of the reactor decreases immensely with increasing reactor volume. If this phenomenon and the different mixing conditions are neglected in the planning of an industrial reactor, there would be a high risk of an accident.

Various experiments have to be executed to obtain information on all involved substances as well as on the process itself. As the process is exothermic and the peroxide tends to decompose, the behaviour of the substances and the process at higher temperatures, for example during a cooling failure, are important to define safety limits. Different equipment is used to gather these information, like the Differential Scanning Calorimetry (DSC), the Thermal Explosion Vessel Test (TEVT), the adiabatic batch reactor ADCII and the reaction calorimeter RC1*e*. The RC1*e* is needed to determine reaction kinetics. These data are required to develop a model to simulate the process. With these simulations recommendations are given concerning the safety of the process for a scale-up from laboratory to pilot scale.

Chapter 2:

Fundamentals

2.1. Introduction

In this chapter the theory of the problems under investigation will be shortly presented for a better understanding. The involved chemicals, a hydroperoxide, a solid and a di-peroxide, must not be described in more detail, as the synthesis reaction was developed by an industrial partner, whose company secrets have to be respected.

The analysed system is a synthesis of a di-peroxide, of which the overall reaction scheme is shown on figure 2.1 below.

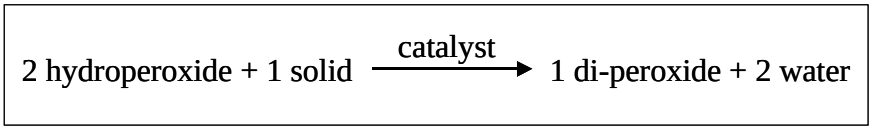


Figure 2.1: Analysed synthesis reaction, overall reaction scheme

As shown in the figure 2.1, a hydroperoxide reacts with a solid, which exists in meta- and para-isomers, under the presence of a catalyst (which is added gradually) to a di-peroxide and water. The catalyst is an inorganic liquid and therefore the system is a solid-liquid-liquid heterogeneous system. For a more detailed analysis of the reaction process, the reaction scheme has to be given in some more detail showing that the di-peroxide is produced in a two-step reaction as follows in figure 2.2 below.

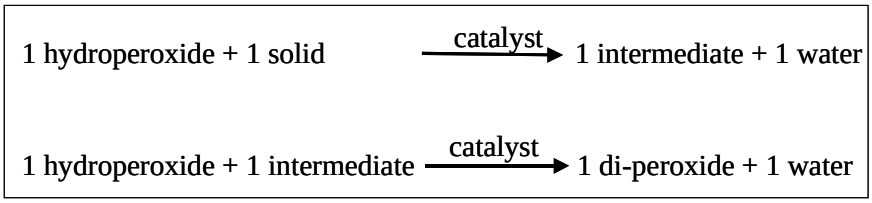


Figure 2.2: Analysed synthesis reaction, side reactions

The process is planned to be operated at a temperature of 15-25°C and an addition time of 20-45min.

As one of the aims of the work was to give recommendations for performing the reaction on pilot scale, after a short introduction to peroxides and heterogeneous systems also an introduction to a scale-up will be given.

2.2. Peroxides

At first, a distinction between inorganic and organic peroxides has to be made. Inorganic peroxides are chemical compounds of the type M_2O_2, where M represents a metallic element, as for example sodium peroxide Na_2O_2. Peroxides are known from alkali metals, alkaline earth metal as well as from Cd, Hg, Zn and a few transition metals [Römpp].

Organic peroxides are all derivates of hydrogen peroxide, H_2O_2, where one or both hydrogens are replaced by an organic group (R-O-O-H or R-O-O-R). Almost all organic peroxides are, due to their facile cleavage of the weak oxygen-oxygen bond, thermally sensitive with a bond enthalpy of ΔH = -125 to -184 kJ/mol. The kinetics of the thermal decomposition are controlled by the nature of the R-groups. Depending on the structure, the temperature activity of organic peroxides varies from below room temperature to above 100°C [Kirk-Othmer].

The first synthesis of an organic peroxide was that of benzoyl peroxide in 1858. Since then many organic peroxides have been synthesized and isolated when industrial interest in peroxides began in the early 1900's. During this period it was found that benzoyl peroxide was an effective bleaching agent for edible oils and for flour [Swern]. Nowadays peroxides are used in a wide range of applications, still as a bleaching agent, but mostly (to approximately 90%) in the plastics industry as an initiator for polymerisation as well as a curing agent and a cross linking agent. In addition, peroxides are used as additives for dermal creams.

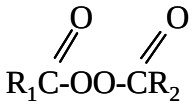
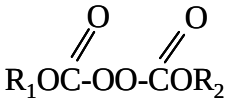
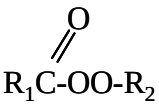
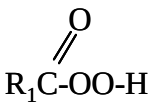
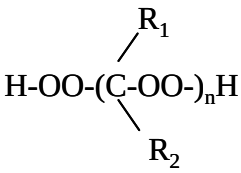
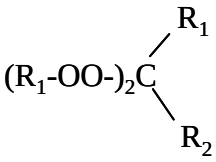
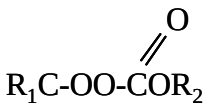
The oxygen-oxygen bond, which is a characteristic of peroxides, is thermally sensitive and energetic. Due to this thermal sensitivity many peroxides tend towards explosiveness. As a rule of thumb, peroxides which contain more than 5% active oxygen, are potentially explosive [Weiberg]. The instability of peroxides has led to many accidents in the chemical industry. As an example, in 1993 50kg of a liquid organic peroxide exploded in Germany. Three men died and the material damage was high [Wandrey].

The characteristic oxygen-oxygen bond contributes to the special properties that all organic peroxides have in common to varying degrees. According to McCloskey [McCloskey] these are:

- Sensitivity to heat; under the influence of temperature the decomposition of peroxides starts.
- Release of heat of decomposition.
- Sensitivity to contamination; contamination by metals or acids for example can accelerate the decomposition of some peroxides.
- Formation of gases and vapours on decomposition for some peroxides.
- Formation of free radicals on decomposition.
- Most peroxides have oxidizing properties.

The characteristic oxygen-oxygen bond of the peroxy-group has a potentially available oxygen atom, from where its oxidizing properties and hazard potential are derived. The common types of organic peroxides are shown in the next table 2.1.

Table 2.1: Different types of peroxides

Peroxide	Structure
Dialkyl peroxides	R_1-OO-R_2
Hydroperoxides	R_1-OO-H
Diacyl peroxides	
Peroxydicarbonates	
Peroxyesters	
Peroxyacids	
Ketone peroxides	
Peroxyketals	
Alkylperoxy carbonates	

This work was executed with a hydroperoxide, which reacts with a solid reactant to another peroxide, a di-peroxide resembling a „double“-dialkylperoxide of the structure R_2-O-O-R_1-O-O-R_2, see also figure 2.1. Hydroperoxides can be separated into two different groups, the alkyl hydroperoxides R_1OOH and the organomineral hydroperoxides $R_mQ(OOH)_n$,

where Q is silicon, germanium, tin or antimony [Kirk-Othmer]. Alkyl hydroperoxides may be primary (R_1CH_2OOH), secondary (R_1CHOOH), or tertiary (R_1COOH). Alkyl hydroperoxides can be liquids or solids, but most of them are liquid. Those with lower molecular weights are soluble in water and are explosive. This water solubility and the violence of its decomposition decreases with increasing molecular weight. Alkyl hydroperoxides can react with or without cleavage of the O-O bond. They react with a variety of compounds to form other organic peroxides [Swern].

Dialkyl peroxides also exist as organomineral peroxides with the formula $R_mQ(OOR)_n$ and R_mQOOQR_m with at least one peroxy oxygen bonded directly to the organo-substituted metal or metalloid Q. The main group of dialkyl peroxides are characterized by the formula R_1OOR_2, where R_1 and R_2 are the same or different primary, secondary, or tertiary alkyl, coalkyl, and aralkyl hydrocarbon or hetero-substituted hydrocarbon radicals. Among the alkyl peroxides the di-t-alkyl peroxides are among the most thermally stable organic peroxides, short alkyl-chain primary dialkyl peroxides are shock-sensitive and explosive. Sensitivity decreases with ascending molecular weight [Kirk-Othmer].

In general, peroxides have to be handled carefully, as most of them are thermally sensitive and start a decomposition easily.

2.3. Heterogeneous systems

All chemical reactions can be splitted in two types: homogeneous and heterogeneous reactions. Homogeneous reactions take place in one phase only, while heterogeneous reactions involve at least two phases. For heterogeneous reactions the most important point is that sufficient mass transfer is provided between the phases for the reaction to proceed as it should. It is still but less important whether the reaction takes place in one, two or more phases, at the interface, or whether the reactants and products are distributed among the phases or are all contained within a single phase [Levenspiel]. The formulation of a reaction scheme and definition of a formal kinetic is therefore much more difficult for a heterogeneous system, as the mass transfer between the phases has to be considered as well. This

mass transfer in heterogeneous systems together with the reaction is also known as macrokinetics while the reaction scheme itself in the (homogeneous) system is named microkinetics.

Different types of heterogeneous reactions are known, as solid-liquid, gas-solid, liquid-liquid and gas liquid systems for two phases reactions as well as a solid-liquid-liquid system where more than two phases are involved. Several theories have been established to describe the mass transfer between the two phases, for example the film theory and the penetration theory. For a safe reactor design it is further helpful to be able to identify, which type the reaction is. Usually, one distinguishes between a slow reaction, fast reaction and an instantaneous reaction [Westerterp]. Finally it has to be considered which type of reactor (for example the continuously stirred tank reactor (CSTR), the batch reactor (BR) or the semi-batch reactor (SBR)) is going to be used in order to construct it in a safe way.

One of the most common models to describe the mass transfer between two phases is the film theory, which was suggested in 1912 by Jablczynski and Przemyski and independently as well in 1923 by Whitman [Brauer]. The penetration theory, also called surface-renewal theory, came later and was first developed by Higbie 1935. Danckwerts as well developed a model for the penetration theory later. Those models were all created for a gas-liquid system but are nowadays all used for a liquid-liquid system as well [Doraiswamy]. The three models will be described shortly.

The film theory:
In the film theory it is assumed, that there is a stagnant film at the interface through which the transport process takes place by simple molecular conduction. The concentration and the velocity are assumed to change in direction of the y-axes only, not in direction of the other axes and not with time. The conditions in the bulk of the phase considered are assumed to be constant. The unique exception is the stagnant film itself, so that the overall driving force is entirely used up by the phenomenon of molecular transport in the film [Astarita].

The penetration theory, Higbie’s model:
Higbies model of the penetration theory assumes that the gas-liquid interface is made up of a variety of small liquid elements. These are brought continuously to the surface from the

bulk of the liquid and vice versa by the motion of the liquid phase itself. As long as it stays on the surface each element of liquid may be considered to be stagnant. The concentration of the dissolved gas in the element may be considered to be equal to the bulk-liquid concentration everywhere when the element is brought to the surface. All surface elements are considered to stay at the surface for the same amount of time. The absorption then takes place by unsteady molecular diffusion in the various elements of the liquid surface [Astarita].

The penetration theory, Danckwerts' model:
The Higbie model was regarded as unrealistic by Danckwerts because it specified the same amount of time of exposure for all elements on the surface. Danckwerts therefore changed the model of 1951 and supposed instead that the chance of an element on the surface being replaced by fresh liquid is independent of the length of time for which it has been exposed. This leads to a stationary distribution of surface 'ages' [Danckwerts].

Both theories, the film theory as well as the penetration theory, end up with the result that the mass transfer coefficient is proportional to the diffusion coefficient. In the film model the mass transfer coefficient depends on the diffusion coefficient as follows:

$$k_i \sim D_i^{2/3} \tag{2.1}$$

For the penetration theory, the Higbie's model as well as the Danckwerts' model, the mass transfer coefficient depends on the diffusion coefficient as follows:

$$k_i \sim \sqrt{D_i} \tag{2.2}$$

Following Baerns [Baerns] the application of either one of the penetration theories or the film theory end in reality in a rather similar result. Therefore the easier film theory is used mostly.

The type of chemical reaction has an influence on the mass transfer. Westerterp [Westerterp] differentiates three types of reactions:

a) Slow reactions:

A reaction is slow with respect to the rate of mass transfer. Characteristic of this type of reaction is that the rate of mass transfer is not enhanced by the occurring reaction and that the reaction mainly takes place in the bulk of the reaction phase.The model is shown in the figure 2.3, with δ denoting the thickness of the film and c_A and c_B the concentrations of the components in one phase and c_{Ai} the actual concentration of the component A in the second phase.

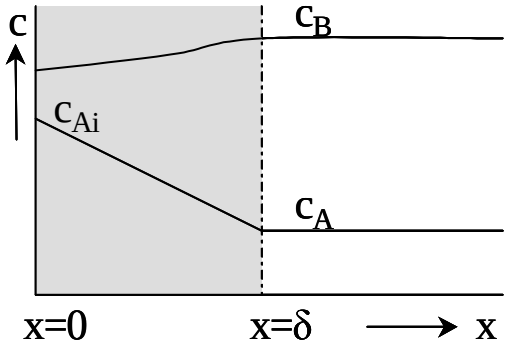


Figure 2.3: Concentration profile in slow reaction according to film theory [Westerterp]

b) Fast reactions:

A reaction is fast when the rate of reaction is so high with respect to the mass transfer, that one reaction partner (for example A) is completely converted near the interface. Then the rate of the mass transfer is enhanced by the chemical reaction

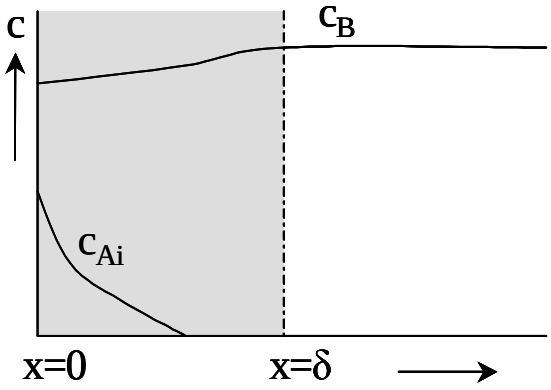


Figure 2.4: Concentration profile in fast reaction according to film theory [Westerterp]

c) Instantaneous reactions:

An instantaneous reaction is so fast that the conversion rate is completely limited by diffusion of both A and B. In the reaction zone A and B do not occur at the same place [Westerterp].

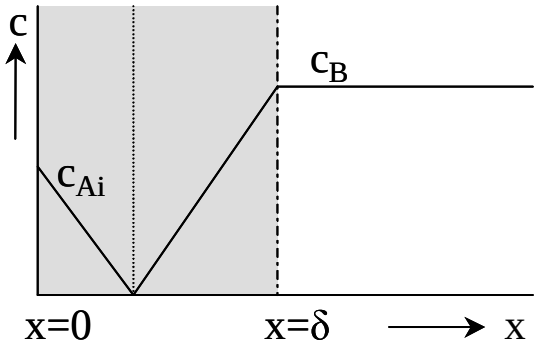


Figure 2.5: Concentration profile in instantaneous reaction according to film theory [Westerterp]

As already mentioned a heterogeneous system is more difficult in respect to a safe reactor design than a homogeneous system because the mass transfer has to be considered as well. For a safe reactor design it is important first to know the type of reaction and preferably reaction kinetics as well. If the system is homogeneous, then different safety criteria for each type of reactor have to be considered. This procedure was well described by Steinbach [Steinbach 4]. For a heterogeneous system a universally accepted criterion for a safe reactor design does not exist. Some attempts have been made for example by Westerterp [Westerterp], Steensma [Steensma], Zaldivar [Zaldivar 1] and Körner [Körner].

2.4. Scale-up

After the successful creation of a new product on laboratory scale, the scale-up to industrial reactors is a great challenge for every engineer or chemist. The ratio of cooling surface to reactor volume (A/V) changes dramatically from the laboratory scale to pilot or even production scale. The ratio of cooling surface to reactor volume (A/V) decreases with increasing scale and therefore the cooling capacity decreases as well. Then, if the heat produced by the chemical reaction cannot be properly removed any more, the temperature of the reacting mixture increases and can finally end up in a thermal runaway. Experiences of the

last two decades showed, that discontinuous plants are more involved in accidents than continuous ones. In spite of this experience, the semi-batch reactor and the batch reactor are more in use in the chemical industry than ever due to their flexible use and economical and multipurpose characteristics [Toulouse].

For heterogeneous reactions no general procedure exists for a scale-up of chemical reactors. Some problems are listed below:

- Kinetic data are peculiar for every reactive system. Often kinetics are masked by transport phenomena and fluid dynamics to the point that sometimes they have no relevance to the process.
- Industrial scale technology are seldom related to laboratory equipment even if industry is full of enlarged laboratory equipment.
- Impurities, aging of the catalyst, corrosion, fouling, safety and environmental aspects can represent a major risk to the success [Donati].

Concerning the scale-up of a process, it is not only important to get a preferably great yield of the product but also an economically profitable process. It is furthermore of great interest to keep in mind all safety aspects to avoid any accidents. This is not easy regarding the decreasing cooling capacity with enlarging scale and the different efficiency of the stirring and therefore an usually worse mixed system with increasing scale. There are various suggestions how to model and how to do a scale-up.

Zlokarnik [Zlokarnik] for example always starts the scale-up (or scale-down) with a dimensional check of the system. According to him, two processes are similar to one another when they take place in a similar geometrical space and when all their characteristic numbers are of the same value. With the help of a successful dimensional analysis a model can be constructed and with this model the system can be assigned to a different scale. According to Zlokarnik [Zlokarnik], this dimensional analysis is helpful for almost all processes in process engineering, like stirring, crushing, emulsifying, etc. For a heterogeneous chemical process the modelling might be difficult due to the heat and mass transfer from one phase into another, of which mechanisms are often unknown.

Shah [Shah] made suggestions for a scale-up of liquid-liquid reactors. According to him it is important to first determine the rate controlling step. Shah worked with the film theory. Therefore reaction could be slow, which means a kinetically controlled regime, or fast, where the reaction takes place in the film between the two phases, or instantaneous, which corresponds to an only mass transfer controlled regime [Westerterp]. With this knowledge, the mathematical model for the liquid-liquid reactor with the differential mass balance and heat balance equations can be set up.

Generally three different steps are important for a scale-up: first the laboratory studies, then pilot plant studies and then the production scale. Although, some processes are even scaled-up directly from the laboratory scale to the production scale. At the last step to the production scale and even before, on the step to the pilot scale, a modelling of the process is very helpful. The models can be divided into the mathematical (for example the deterministic and probabilistic models as well as the dynamic and steady state models), the physical and the chemical models [Euzen]. But this distinction remains formal, in practice, an individual model has to be found for each system.

The best practice for a safe scale-up will always be an inherently safe system.

Chapter 3:

German regulation TRAS 410

3.1. Introduction

The procedure of analysing and evaluating the hazard potential of the investigated process was based on TRAS 410 [Anlagensicherheit], which is a German technical regulation for process safety. This technical rule has to be applied by anyone who wants to run a chemical plant in Germany, which needs a permit to operate. The straightest way of performing the necessary investigations is to follow the schemes. Based on TRAS 410 the hazard investigation begins with the safety assessment of the pure substances and their mixtures followed by the evaluation of the desired process under normal operating conditions. The corresponding scheme can be seen on figure 3.1. For the evaluation of safety criteria for the desired reaction, it is first necessary to evaluate the reaction conditions. The reactor-type (BR, SBR, CSTR) has to be specified as well as the amount of substances, the time of addition, the reaction temperature and pressure and the concentrations.

For the first investigations of the substances fast screening-tests are usually applied. These could for example be tests with differential scanning calorimetry (DSC). It has to be proven that all substances and intermediates are thermally stable in the temperature range of the process conditions.

After the evaluation of the substances the process itself has to be examined. Therefore the desired reaction has to be evaluated, including all side and consecutive reactions. Important results from this investigations of hazards under operating conditions are for example the adiabatic rise in temperature ΔT_{ad} of the process, the accumulation risk in semi-batch reactions, the heat produced by the reaction and the onset temperature of the decomposition of product or educt. Further it is important to know if any gas is produced during the reaction to be able to avoid an impermissible high pressure in the reactor.

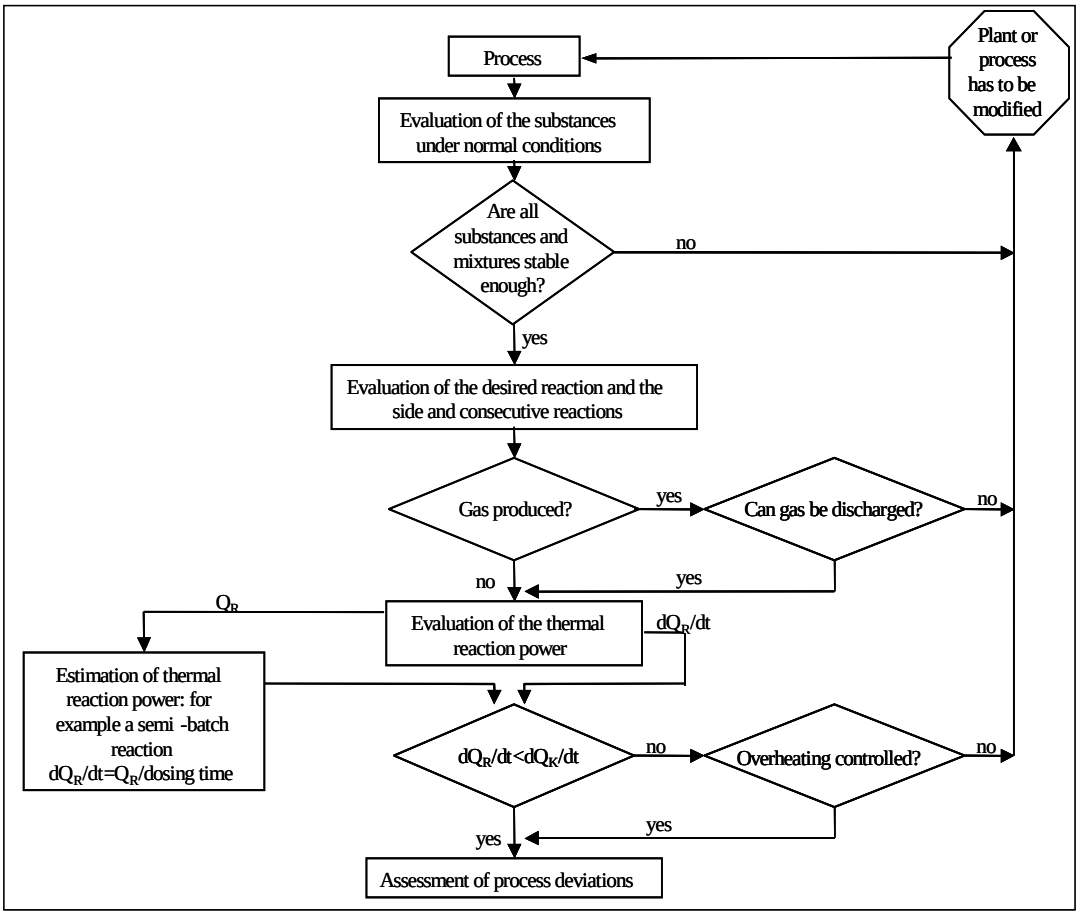


Figure 3.1: Iterative assessment of the process under normal operating conditions

After the evaluation of safety criteria for the process under normal operating conditions, a closer look at possible process deviations and their consequences for the safety has to be taken. Possible deviations have to be foreseen and their consequences discussed. For some reactions already very small changes can have a great effect, or even cause a thermal runaway. The TRAS 410 [Anlagensicherheit] includes a list of possible changes in the reaction process, which might influence the process safety. Examples are different concentrations of the educts, a faster addition of a reaction partner for a semi-batch reaction, a different reaction temperature, a higher pressure or a contamination of the reactor.

After the identification of these process deviations, it has to be evaluated if the safety criteria are strict enough to lead the system to a safe condition after the failure. If not, the process has to be changed. This procedure is shown in figure 3.2.

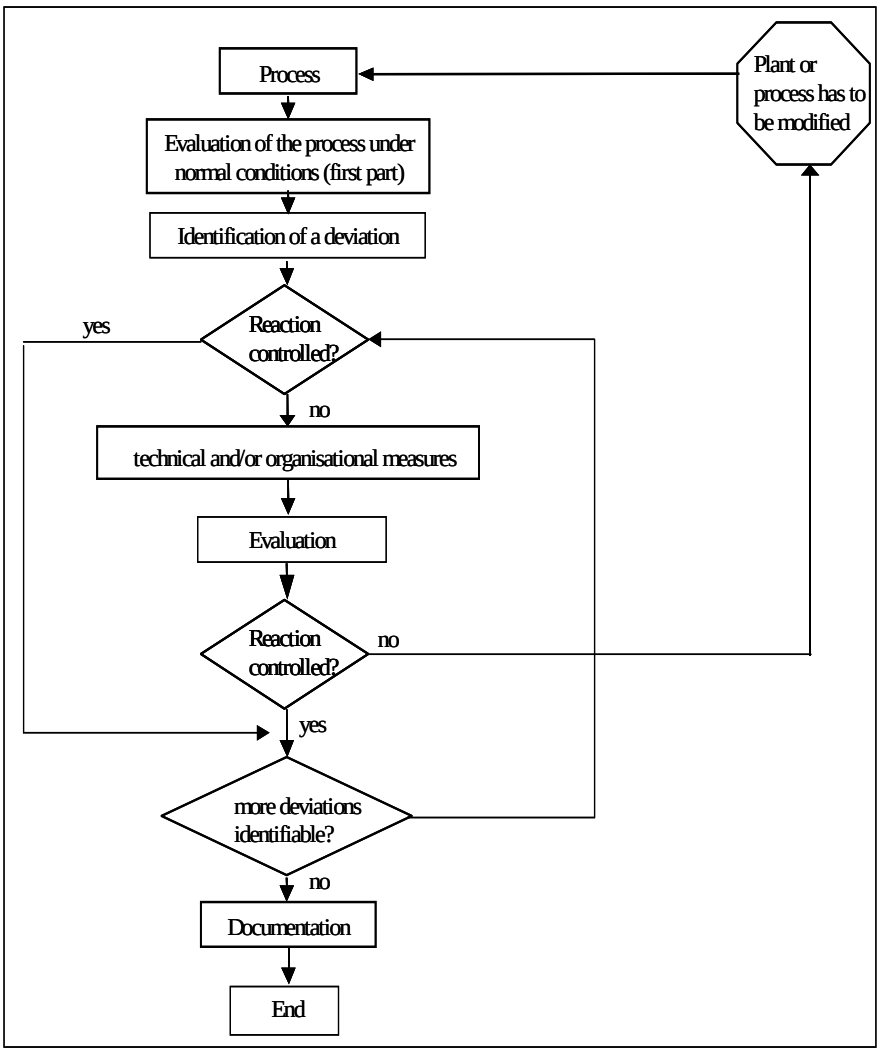


Figure 3.2: Iterative assessment of process deviations

This procedure has to be reiterated for any possible deviation of the process and it has to be checked, if safety is always ensured. If a critical situation might occur due to the deviation, certain measures have to be taken to prevent any dangerous situation. These could be either preventive or constructive in nature. A constructive measure could be a pressure resistant construction or a pressure relief system for example. A preventive measure could be an emergency cooling system, a system to stop the reaction very quickly, for example addition of an inhibitor, a good process guidance or even organisational measures. The measures to be taken depend on the expected failure and the process.

3.2. Application of the TRAS 410-procedure to a reaction system

Various reaction systems, for example polymerisation, may cause several problems at different steps of the analysis. Therefore, proceeding for the analysis of the process under normal operating conditions will be explained stepwise. The first part of the TRAS 410 is shown in figure 3.3.

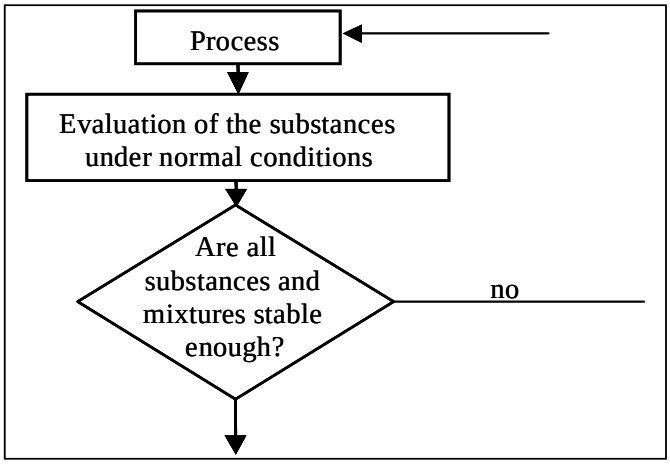


Figure 3.3: First part of TRAS 410

These first analysis of the substances can be performed with the help of the DSC, TS^U and the TEVT for example (see chapter 4 for the explanation of the apparatuses and methods). In this first step it is important to estimate the hazard potential of the pure substances. Therefore physical properties of the substances like the decomposition enthalpy, the onset temperature, rise in pressure during the decomposition, the maximum temperature for example are determined. With the help of these data, first safety criteria for example the Time to Maximum Rate (TMR) or the maximum temperature according to the 100K-rule can be calculated (for the explanation of the safety criteria see chapter 4). If the mixtures and substances are stable enough, the next step follows, otherwise the process has to be changed.

After the substances the reaction itself has to be investigated as can be seen in figure 3.4.

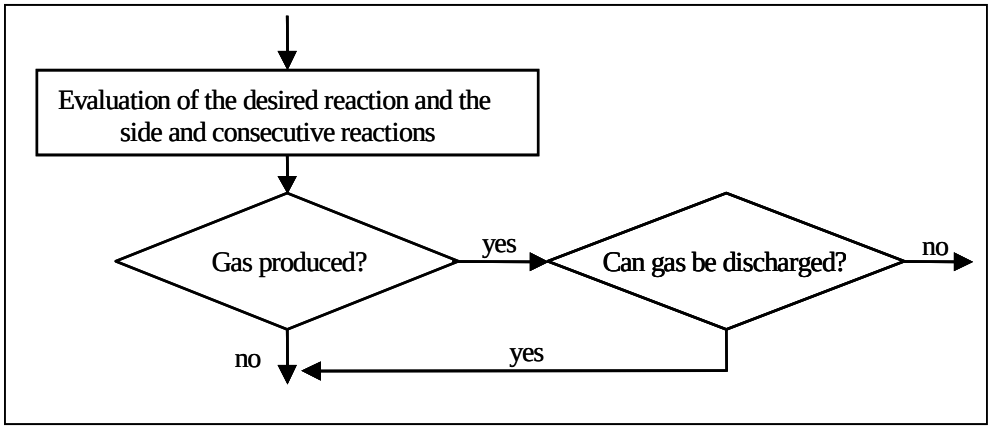


Figure 3.4: Second part of TRAS 410

In this part of the TRAS 410 the reaction itself has to be analysed. For this purpose a reaction calorimeter is mostly used, e.g. the reaction calorimeter RC1*e* from Mettler Toledo, which was used in this work (the RC1*e* will be presented in chapter 4.2.2.). For consecutive reactions and also for the analysis of a possible runaway reaction, an adiabatic calorimeter like the ADC II, which was used in the work presented, can be helpful. Especially important is the analysis if there is a production of gas during any reaction as the gas might cause a steep rise in pressure in the reactor and may lead to its rupture. If there is no development of gas, or the produced gas can be discharged, no change in the process is necessary and the third step follows.

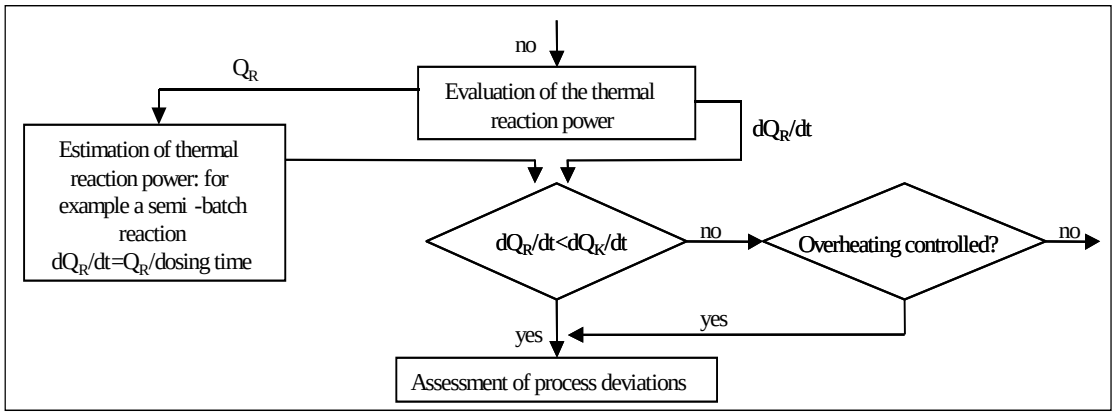


Figure 3.5: Third part of TRAS 410

For the procedure of the last part of the TRAS 410 concerning the process under normal operating conditions, the data of the experiments in the reaction calorimeter have to be analysed further. The total heat of the reaction released over time has to be determined and compared with the possible heat conduction of the cooling system. If the cooling system is sufficient for the desired reaction that even a possible overheating can be controlled, the evaluation of the normal process is ended, otherwise the process has to be changed and analysed again.

After the evaluation of the process under normal operating conditions, possible process deviations like a cooling failure, wrong addition or a too high or too low process temperature and their effects on the process have to be analysed. If these effects cannot be controlled, the process has to be changed and the procedure has to be reiterated again.

Chapter 4:

Materials and methods

4.1. Methods for characterisation of the pure substances

The pure substances were first analysed in order to report the rise in temperature and pressure under conditions of increasing temperature. Three different methods were used, the differential scanning calorimetry (DSC) for the analysis of the released heat and the thermal explosion vessel test (TEVT) as well as the thermal screening unit (TS^U) to characterise explosibility hazard and developing pressure.

4.1.1. The differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) and also the differential thermal analysis (DTA) are well known and often used in safety technology. As these methods are described in literature in detail, see: [Hemminger 1], [Hemminger 2], [Höhne], only a short explanation will be given here. Both names are often used synonymously, although their measuring system is different. Usually the measured parameter in the DTA is the difference in temperature (ΔT) between the sample and the reference, while the measured parameter in the DSC is the differential change in the heat flow ($\Delta dQ/dt$). In this work the DSC 821 from Mettler Toledo, which measuring principle will be explained in the following paragraph, was used.

Höhne [Höhne] gives a definition of the DSC as follows: „Differential Scanning Calorimetry (DSC) means the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program“. The DSC 821 from Mettler Toledo can give rather quickly information on the temperature range of the decomposition, the enthalpy, the onset temperature and the time to maximum rate of the sample.The system consists mainly of an oven, various thermocou-

ples, a cooling system, a measuring system and a computer. For a measurement in the differential scanning calorimetry the sample to be analysed and a reference made of an inert material are placed in the oven. The oven is heated and the increasing temperatures of sample and reference are measured. The difference in temperature between the sample and the reference gives an information of the developing or consumed heat during the reaction. With the help of a calibration of the DSC 821 before starting the experiment, the signal heat release rate dQ/dt can be calculated from ΔT. The DSC 821 is shown schematically in figure 4.1.

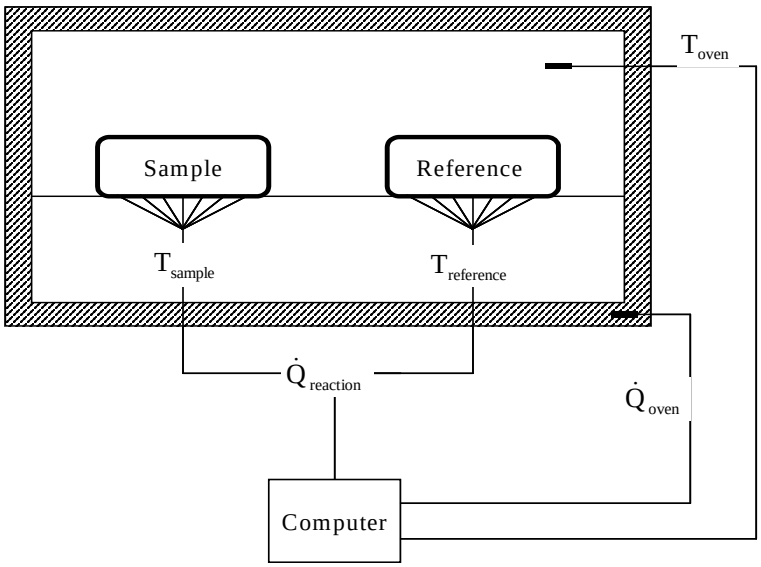


Figure 4.1: Schematically presentation of the DSC

Basically there are two different ways of operating the DSC. First is the temperature programmed method, where the oven is heated up with a constant heating rate, usually between 0.5K-20K/min. This method gives information on the temperature range, where the reaction of the sample takes place; the onset temperature and the reaction enthalpy. Further a first safety criteria could be calculated, the so called 100K-rule which was first mentioned by Hofelich [Hofelich]. Hofelich characterised it as a rule which is easy to apply and therefore often used in the chemical industry. According to this rule, „an exothermic process that shows an observable onset, the point where the temperature is first significantly different from the baseline in a DSC scanning experiment performed with a heating rate of 10K/min, at least 100 Kelvin higher than the recommended manufacturing process temperature will not pose a thermal hazard under plant operating conditions“. This rule was later

restricted to „normal“ substances which means that they have a normal shift in the peak maximum temperature. In a first and fast analysis, shifts are regarded as „normal“ if the maximum temperatures (the peak-maxima) of two experiments at heating rates differing by a factor of 10 do not differ more than 40K. For a closer and precise analysis, more than two scanning experiments with varying heating rates are characterised. If then the following condition is fulfilled: $d\ln(HR)/dT > 0.057K^{-1}$; the 100K-rule may be applied.

The second possibility of operating the differential scanning calorimetry is the isothermal method. In isothermal measurements the oven temperature is kept constant at a certain value. These experiments are not performed as fast as the temperature programmed measurements, but offer further information. As in the temperature programmed test the total heat output due to a physical or chemical transition process is given. Further, the peak shape of the isothermal tests provide a unique indication on the kinetics and finally the time to maximum reaction rate can be estimated [Steinbach 4]. The time to maximum reaction rate, or shorter and also well known as TMR, is another safety criteria. It is equivalent to the time from a failure of the cooling system to the maximum rise in temperature of the system. The TMR can be deduced from Semenov’s thermal explosion theory [Semenoff]. For the calculation of the TMR a zeroth order chemical reaction in a batch reactor under adiabatic conditions, that is no heat exchange with the surroundings, and a temperature dependence of the reaction rate according to the Arrhenius relationship are assumed. Then it is possible with the help of Frank-Kamenetskii [Frank-Kamenetskii] to calculate the time necessary to reach the point of the highest reaction rate according to the following equation:

$$TMR = \frac{c_p \cdot R \cdot T_0^2}{E \cdot \dot{q}_0} \tag{4.1}$$

The temperature T_0 in this equation denotes to the isothermal temperature, c_p is the heat capacity of the sample, $\dot{q}_0$ the maximum heat release rate and E/R is the activation temperature. This activation temperature has to be calculated first before the TMR can be determined. The activation temperature cannot be calculated directly from the isothermal tests in the DSC. But it is assumed that the measured heat output rate may be directly attributed to the chemical heat release rate, which depends exponential on the temperature

according to Arrhenius. Therefore a plot of the measured maximum of the heat release rate in a logarithmic scale over the reciprocal value of the measuring temperature in absolute degrees Kelvin should yield in a straight line. The slope of this straight line is equivalent to the activation temperature E/R, according to the following equation [Steinbach 3]:

$$\ln(\dot{q}|_{max}) = \ln(\nu_a \cdot V \cdot \Delta_R(h \cdot r_{max,\infty})) - \left(\frac{E}{R} \cdot \frac{1}{T_{iso}}\right) \quad (4.2)$$

Now the activation temperature E/R [K] can be determined. With this information the TMR can be determined and the temperature for a TMR of 24h as well. This calculation can be approximated with the help of the plot ln(TMR) versus $1/T_{iso}$, which gives a rather straight line and allows an estimation for all values of TMR or isothermal temperature. The TMR itself or, better, the temperature where the TMR is equivalent to 24h is another safety criteria deduced from experiments in the DSC. The TMR should be equivalent to 24h as then there is usually enough time to respond to a process failure, like breakdown of the cooling system. Then it is well possible to avoid a thermal runaway.

4.1.2. The thermal explosion vessel test (TEVT)

The Thermal Explosion Vessel Test (TEVT) is a former UN-test and was invented for tests with peroxides. A picture of it is found in figure 4.2, a scheme in figure 4.3. The TEVT consists of a pressure proven container, which is heated up during the experiment. Temperature is measured with a resistance thermometer Pt100 at four different points: in the oven around the test cell, in the jacket of the test cell and twice in the test cell, in the sample, and in the gas phase above the sample. Further, the pressure is measured and, at the moment of a detectable decomposition, the measuring frequency is increased to obtain a reliable information on the rise in pressure, so that the maximum value of dp/dt and the maximum difference in pressure Δp as well as the characteristic parameter $dp/dt \cdot \Delta p$ (effect of pressure) are obtained. As stated by Brown [Brown] the value max $dp/dt \cdot \Delta p$ is a good criteria to determine the risk of handling an explosive substance. Further, there is a rupture disc with a

set value of 100bar. In case of a too high pressure it will burst. Usually 5g of sample are weighed in a glass test cell and placed inside the container. The container is then placed inside a hot wind chamber and heated up with a heating rate of 18K/min.

Figure 4.2: Photo of the TEVT

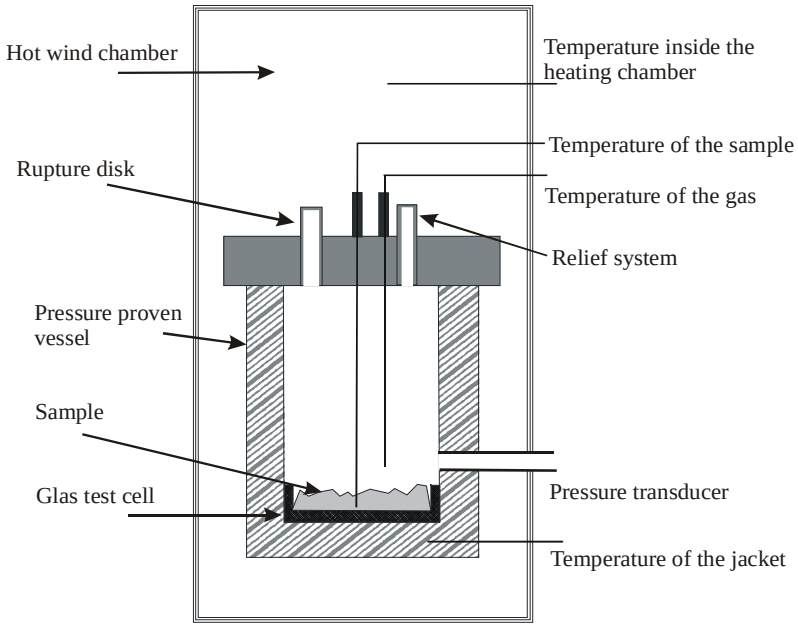


Figure 4.3: Schematically representation of the TEVT

In the first edition of the Guideline from the United Nations „Recommendations on the Transport of Dangerous goods“ [Nations 1] the TEVT was still listed as a possible test for peroxides. By now, only similar tests are mentioned. These are the Dutch pressure vessel test and the United states pressure vessel test, both of which also measure the rise in pressure under defined confinement and rising temperature. In these tests, the developing pressure is not recorded. But they are equipped with rupture disc. The vent area can be varied with the help of orifice plates with diameters from 1.0 to 24.0mm. The rupture of these disks is analysed at the different openings [Nations 2].

4.1.3. The Thermal Screening Unit (TS^U)

The thermal screening unit TS^U was developed by HEL. In this work the rise in temperature and pressure were simultaneously analysed during the decomposition of the substances.

The TS^U has a test cell, which consists of a small bomb of approximately 8ml content and which is stored in a kind of pressure proven heater during the test, a photo of it is shown in figure 4.4 and a scheme in figure 4.5. In principal, there are two methods of operation for the TS^U. The first mode is a ramped test, where the substance is heated with a constant heating rate, and the other is kind of "pseudo-isothermal" mode of operation. But in this second mode, the test cell has to be placed in the oven already at room temperature and it is then quickly heated up and finally kept at an isothermal temperature. The temperature of the oven, the temperature in the test cell and the pressure are measured during the experiment. The temperature range is from ambient up to 400°C, the pressure range up to 200bar. Test cells are available in stainless steel, hastelloy, tantalum, titanium and also in glass. The advantage of this method is that not only the temperature but also the pressure is recorded. Concerning the temperature, information on the maximum temperature, the onset temperature of an exothermic reaction, the rate of temperature rise and the time from exothermal initiation to maximum rate is obtained. Furthermore information on the rate of pressure rise and on the maximum pressure is determined.

Figure 4.4: Photo of the TS^{U} and sample cell

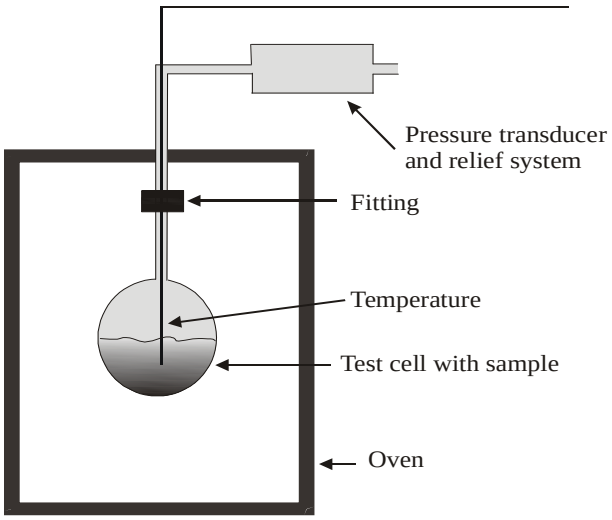


Figure 4.5: Schematically representation of the TS^{U}

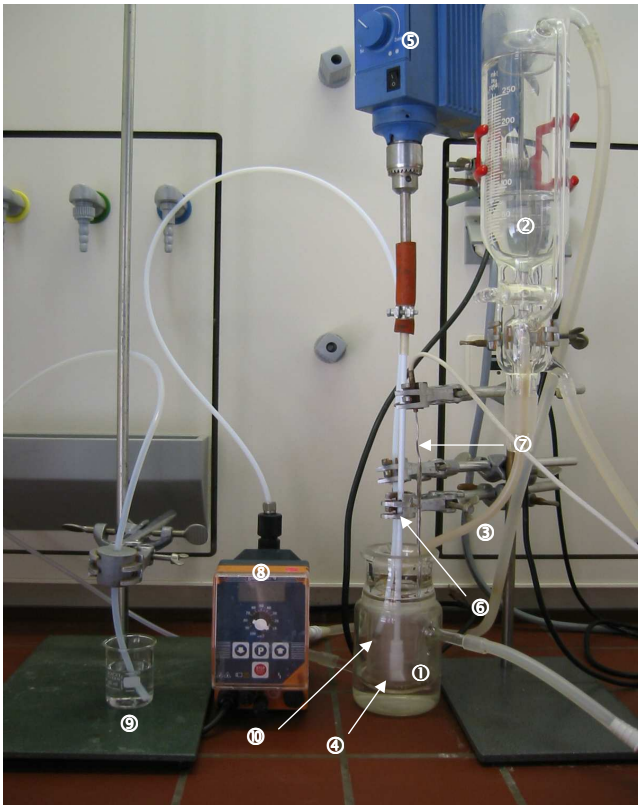
4.2. Methods for the characterisation of the process under normal operating conditions

The process under normal conditions was first analysed in a small laboratory glass reactor of approximately 250ml. After positive results in the small reactor, experiments were also performed in the RC1*e* from Mettler-Toledo.

4.2.1. The Mini-Laboratory-Reactor

The aim of using the mini-laboratory-reactor was to do the first tests on very small scale and therefore minimize the hazard potential. The vessel used was a jacketed glass reactor of 250ml in volume. It was operated at a constant jacket temperature of 15°C. It was equipped with a stirrer and a thermocouple and a tube for the addition of the catalyst. Further there was a cooled vessel filled with water for an emergency quenching. The hydroperoxid and the solid were charged first and stirred, while the temperature was kept constant. Then the catalyst was added.

In figure 4.6 the mini-laboratory-reactor is shown and its components are explained thereafter. The reaction takes place in the jacketed glass-reactor of 250ml (1). Above the reactor is the cooled vessel filled with water (2) for an emergency quenching and a pipe into the reactor (3). Further there is a stirring motor (5) and a pitch-blade stirrer (4). The stirrer is fixed with a clamp (6) above the reactor. Also fixed with a clamp is a Pt100-thermocouple (7). Finally there is a pump (8) from Prominent to add the catalyst (9) with a tube (10) to the components already inside the reactor.



Key:

(1) = glass-reactor of 250ml
(2) = cooled vessel with water
(3) = pipe into the reactor
(4) = pitch-blade stirrer
(5) = stirring motor
(6) = clamp
(7) = Pt100-thermocouple
(8) = pump from Prominent
(9) = catalyst
(10) = tube

Figure 4.6: Photo of the mini-laboratory-reactor

4.2.2. The reaction calorimeter RC1*e*

For a larger scale than the small laboratory reactor the RC1*e* from Mettler Toledo was used. The detailed description of the RC1*e* can be found in the respective Manual [RC1 Manual], and therefore the method will only be described here shortly. The RC1*e* is a heat flow calorimeter. The heat produced by the reaction is calculated with the help of the temperature difference between the cooling temperature in the jacket and the temperature inside the reactor. The RC1*e* can be operated in an isothermal, an isoperibolic and even in an adiabatic mode. The investigated process was operated in an isothermal, a semi-batch mode. The RC1*e*-system was equipped with the reactor vessel AP01, a thermostat, propeller stirrer with baffles, a measuring system, an addition system (including a pump and a balance) for the catalyst and a personal computer with printer. With Pt100 thermocouples the temperature inside the reactor and the temperature of the jacket are continuously measured.

Further there is a calibration heater inside, which is used for the determination of the heat transfer coefficient of the system. To avoid any catalytic effects, all inserts were out of or covered with glass.

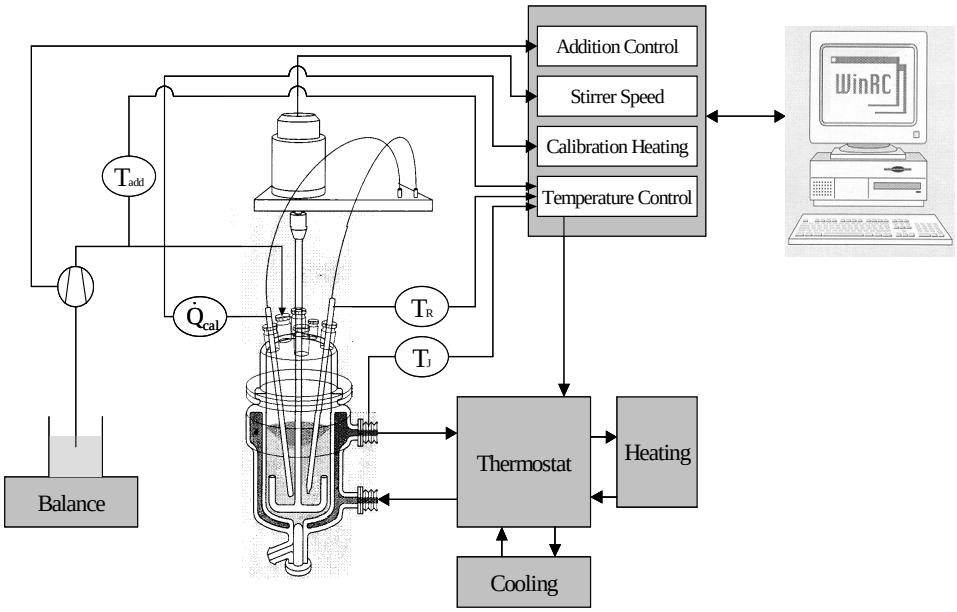


Figure 4.7: Schematically presentation of the RC1*e*

For the evaluation of the measured data the following equations are relevant:

1. The conductive heat flux (through the jacket):

$$\dot{Q}_W = k_W \cdot A \cdot (T_J - T_R) \tag{4.3}$$

In order to calculate the conductive heat flux the overall heat transfer coefficient is determined with the help of a calibration while the driving temperature difference (T_J-T_R) is continuously measured. The heat transfer area is approximated by a model which takes into account both tromb formation and increase of wetted surface by the volume increase due to the dosage. The calibration should be performed before and after the reaction.

2. The convective heat flux caused by the addition:

$$\dot{Q}_{add} = \dot{m}_{add} \cdot c_{p,\,add} \cdot (T_{add} - T_R) \tag{4.4}$$

The temperature of the added substance is measured shortly before the entrance into the reactor.

3. Accumulation:

$$\dot{Q}_{accu} = (m \cdot c_p)_{total} \cdot \frac{dT_R}{dt} \tag{4.5}$$

This equation considers not only the heat accumulation of the reaction mixture, but also of the components of the RC1*e*. The heat capacity of the reaction mixture was determined with temperature ramps of 0.5K/min for 10 minutes before and after the reaction at two different temperatures each. As in this work the RC1*e* was operated isothermally, there was no accumulation.

4. Heat loss:

$$\dot{Q}_{loss} = \alpha \cdot (T_R - T_{env}) \tag{4.6}$$

This equation considers the heat loss to the environment. It is only necessary at very high or very low temperatures. In the analysed case the reaction temperature was almost equal to room temperature or below so that equation 4 does not have to be considered.

5. Chemical heat flux:

$$\dot{Q}_{chem} = (-\Delta_R H) \cdot V_R \cdot r \tag{4.7}$$

The chemical heat flux is calculated with the help of the heat balance using above terms:

$$\dot{Q}_{chem} = \dot{Q}_{accu} - \dot{Q}_W - \dot{Q}_{add} + \dot{Q}_{loss} \tag{4.8}$$

In the present work the accumulation and the heat loss did not have to be considered and the equation is therefore:

$$\dot{Q}_{chem} = -\dot{Q}_W - \dot{Q}_{add} \tag{4.9}$$

With the RC1*e* Software Elvdata the data can be evaluated further, a baseline is fixed and the area, where the heat release rate differs significantly from the baseline is integrated. From this integral the reaction enthalpy and the thermal conversion can be calculated. The thermal conversion is calculated with the help of the sum of all heat released at the present moment divided by the sum of all released heat at the end of the reaction, as in the presented equation:

$$X_{therm} = \frac{\int_0^t \dot{Q}dt}{\int_0^\infty \dot{Q}dt} \quad (4.10)$$

If there is only one reaction to be analysed in the system, thermal and analytical conversion should be identical and the thermal conversion can be used instead of the analytical conversion. This is helpful as the thermal data are obtained much easier, than the analytical ones.

4.2.3. The HPLC

HPLC is short for high pressure liquid chromatography or high performance liquid chromatography, which is the more common name nowadays. It is a well used system to separate and analyse a sample [Bauer]. For the separation, HPLC is operated with a mobile and a stationary phase, which is packed in a column. The sample should be soluble in the mobile phase and is transported by it over the stationary phase in the column. Based on the difference in polarity of the two phases the sample is separated by interactions between the mobile and the stationary phase [Wippo].

The separated components of the sample are then analysed in a detector and can be quantified after a calibration. Most common are UV-detectors, further possibilities are ionisation-detectors, the combination with mass spectroscopy etc. [Bauer], [Wippo].

In this work, HPLC, 1100 series, from Agilent was used. It consists of a vacuum degasser, a quartenary pump, an autosampler, an oven for the column and a diode-array-detector. It was operated with a reversed-phase column from Interchim. The mobile phase was a mixture of water and acetonitrile and operated in a gradient program. The complete analysing program is found in the appendix.

4.2. Methods for the characterisation of process deviations

Possible process deviations are in most cases caused by ineffective cooling, which can lead to uncontrollable rises in temperature and pressure. This uncontrolled rise in temperature was first analysed in a small adiabatic batch reactor of laboratory scale and then the rises in temperature and pressure were analysed in the ADC II.

4.2.1. The adiabatic batch reactor

The equipment for the adiabatic batch reactor consists of a glass dewar, a stirrer, a metering unit, two Pt100 thermocouples and a computer for on-line data recording. The dewar resembles a thermos flask, which means, very limited amounts of heat are lost through the wall. The walls are metallised and it has a volumetric capacity of 0.5l. The first component of the reaction is charged in the dewar at the beginning of the preparation of the experiments. The second component is added to a vessel above the reactor for a manual addition. When both reactants show approximately the same temperature, the second substance is added at high rate and the experiment started. During the preparation and the experiment, the mixture is continuously stirred. The temperature is recorded until when it stops to rise.

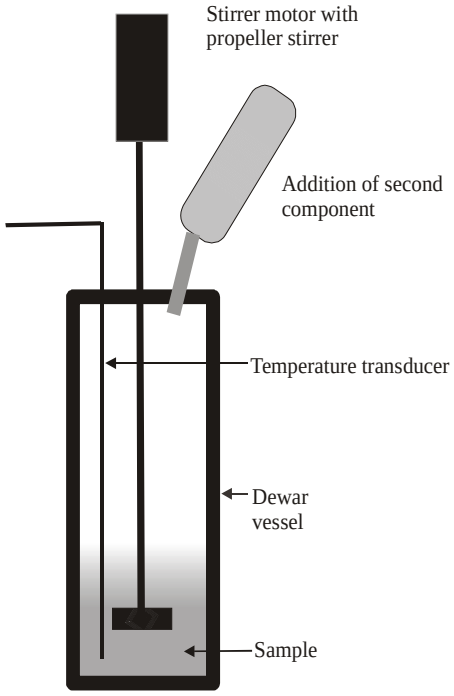


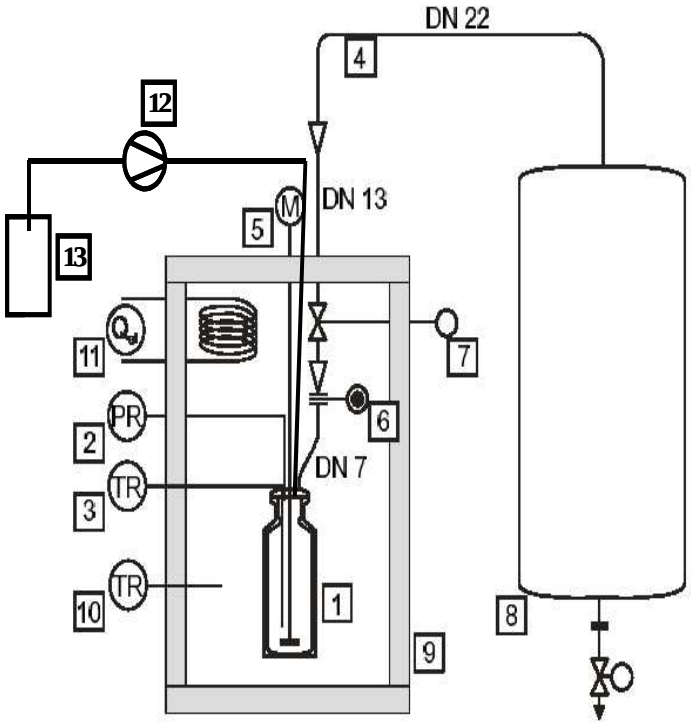
Figure 4.8: Schematically presentation of the adiabatic batch reactor

4.2.2. The ADC II

The ADC II is an adiabatic pressure-calorimeter from Chilworth Technology Southampton/England. This calorimeter is designed to characterise chemical reactions under runaway conditions. The development of pressure and temperature are measured. The construction can be seen in figure 4.9, a picture of the inside of the oven in figure 4.10.

The "heart" of this apparatus is the metal dewar flask of 1.1l volume (number 1 in the figure 4.9). This dewar flask is constructed like a thermos-flask, with double-walls and an evacuated jacket. The inside diameter is 85mm. In addition there is an PFA-coating inside to eliminate any catalytic effects from any metal. The dewar flask is pressure-proven up to 25bar and closed with a non-insulating lid. The temperature and pressure inside the dewar are measured (numbers 2 and 3). It is stirred with a pitch-blade stirrer (number 5). The dewar lid is also equipped with a venting pipe, which ends in a 120-litre catch tank. The venting process is controlled by a fast pneumatic-driven ball valve (numbers 6, 7 and 8). The dewar flask is placed inside an oven (number 9). The oven is heated (number 11) and its temperature is measured and controlled to follow the temperature of the reaction mass (number 10). During the adiabatic experiment, the temperature of the sample inside the dewar flask and the oven are taken and the temperature of the oven is adjusted in a way, that it is always almost equal compared to that in the dewar flask. Therefore no loss of heat from the dewar can be assumed.

An extra equipment for the addition of the catalyst (number 13) is needed for the experiments. Therefore a steel tube with PFA-tubes insides and with a valve to hold the pressure was connected to the dewar flask. The addition was done together with a Prominent pump (number 12), usually within a few seconds.



Key:

(1) = Dewar flask
(2) = Pressure transducer
(3) = Temperature transducer
(4) = Venting pipe
(5) = Stirring motor with stirrer
(6) = Connection to venting pipe
(7) = Pneumatic driven ball valve
(8) = 120l-catch tank
(9) = Oven
(10) = Temperature transducer
(11) = Heating
(12) = Prominent pump
(13) = Catalyst

Figure 4.9: The ADC II

Figure 4.10: Photo of the ADC II inside the oven

Chapter 5:

Results:
Analysis of the organic peroxide synthesis

5.1. Analysis of the pure substances

Following the procedure of analysing a new developed process according to the TRAS 410, for a first estimation of the hazard potential of the synthesis reaction, all involved substances have to be analysed in pure form. After an introduction to the problems occurring at these analysis, the results of the experiments will be shown. The educts, hydroperoxide and solid, as well as the product di-peroxide were analysed in the TEVT and the DSC, partly also in the TS^U. The formed intermediate was also analysed in the DSC, even if it could not be isolated. Consequently, it was measured in mixture with the hydroperoxide and the already formed di-peroxide. The chapter will finish with a recommendation on handling the substances in pure form.

5.1.1. Introduction

For the recommendations on a safe handling of a substance, usually measurements in the DSC are performed first. In most cases, these experiments give in relatively short time reliable results. But in the presented work the majority of the analysed substances were peroxides and they have characteristics which complicate the DSC experiments. Peroxides are highly exothermic and reactive and their decomposition can well be catalysed by different substances, as for example the steel of the sample cells of the DSC. As the pressure resistant sample cells used were made of steel, this catalytic effect caused problems. The isothermal measurements in the DSC were due to this catalytic effect not as reliable as usual and therefore different ways to determine the TMR for the peroxides had to be found.

Also the experiments in the TS^U were influenced by the catalytic effect of the steel. For the TS^U test cells out of glass were provided, but the Pt100 plunging into the sample to record the temperature also caused a catalytic effect. The same phenomenon is found in the TEVT, were the sample cell is also out of glass, but the recording Pt100 can also have a catalytic effect. An attempt had to be made to analyse and evaluate all the data with the catalytic effect in a sensible form.

5.1.2. The hydroperoxide

As common in safety investigations the hydroperoxide was first analysed in the DSC. It was started with dynamical measurements to first specify the temperature range where the decomposition of the hydroperoxide takes place. Tests were performed at four different heating rates, 1K/min; 2.5K/min; 5K/min and 10K/min. The results can be observed in figure 5.1. The 100K-rule was applied and gave 5°C as a maximum temperature for a safe handling, due to an onset temperature of T_{onset} = 105°C at the 10K/min test. In all four measurements there were two peaks observable which might indicate a consecutive reaction as mentioned by Keller et al. [Keller]. In the presented case the reason is more likely to be found in a complex decomposition reaction. It is further well possible that the steel of the test cells catalyses the reaction, because a measurement with a glass test cell, performed by the industrial partner, did not show this shape. The 100K-rule was of course calculated with the first peak. The slope $d\ln(HR)/dT_{max}$ was calculated to 0.0663 K^{-1} > 0.057 K^{-1} and the 100K-rule could therefore be applied. The decomposition enthalpy is very high, an average value out of 8 tests at different heating rates (from 1K/min to 10K/min) of $\Delta_R h$ = -172.8kJ/mole was calculated. Already these first tests showed an enormous hazard potential of the hydroperoxide. The calculated maximum temperature due to the 100K-rule of 5°C shows that the process, operated at higher temperatures than 5°C, might cause problems. According to these first tests the temperature range where a measurable decomposition takes place is between 105°C and 200°C. But the substance required further tests, due to the low thermal onset temperature.

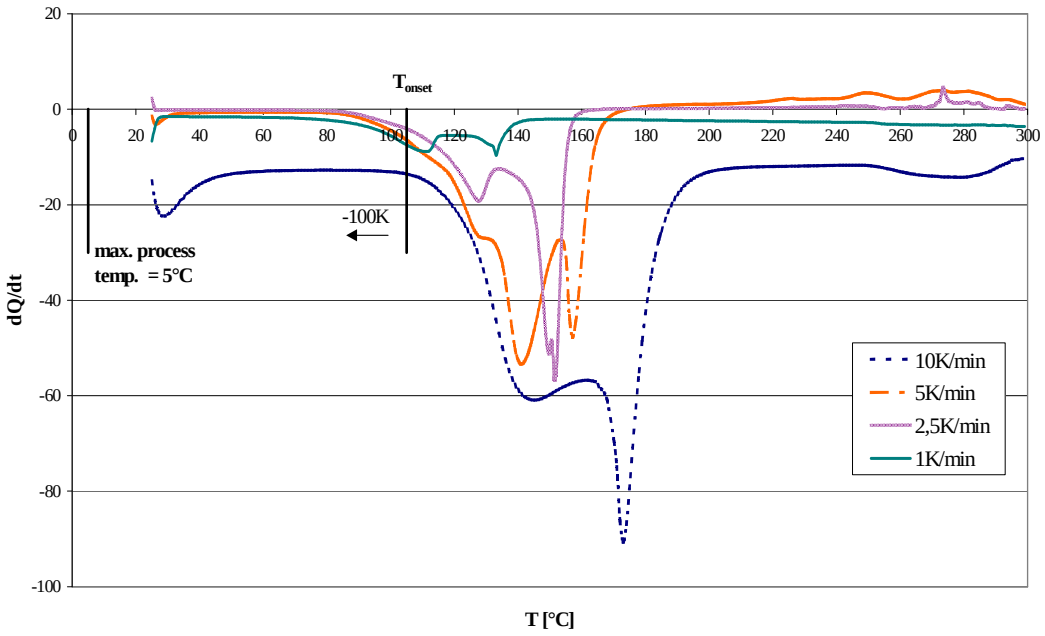


Figure 5.1: Dynamical tests of the hydroperoxide

After the dynamical tests, isothermal tests were performed at different temperatures (135°C, 140°C, 145°C, 150°C). Unfortunately it was difficult to get reasonable results. Either the hydroperoxide did not react completely during the isothermal test or it reacted so fast that it was impossible to record the complete decomposition by the DSC. Several attempts to improve the results, for example with a passivation of the sample cell or an isothermal storage test as described by Grewer [Grewer] were unsuccessful. For the isothermal storage test, several samples of the same amount are stored at a defined temperature. The concentration of the samples over time are measured by analysing each sample after a defined interval in a temperature programmed DSC. This method failed, as the decomposition of the hydroperoxide is too fast, if once started.

The few isothermal results at 140°C, 145°C and 150°C which seemed reasonable, were evaluated. The activation temperature must be calculated first before the TMR can be determined as explained in chapter 4.1.1. The activation temperature E/R [K] was determined to $1.28 \cdot 10^4$ K. The corresponding diagram is shown in the appendix A.1.

With the information of the activation temperature the TMR can be determined and the temperature for a TMR of 24h as well. The temperature where the time to maximum rate (TMR) is equivalent to 24h was calculated to 39°C.

As the isothermal data for the determination of the TMR did not seem very reliable, a second method was used to determine the TMR of the decomposition of the hydroperoxide. Following Keller et al. [Keller] and Pastré [Pastré], the TMR can also be estimated from dynamical DSC-measurements. For this estimation, the activation energy is first estimated to E=50kJ/mole, which is a conservative estimation as most decomposition reactions have higher activation energies. It is further assumed that the heat release rate at the onset point dq/dt_{onset} is of the order of 20W/kg [Keller]. Following then Arrhenius by assuming an exponential dependency of the temperature on the heat release rate, it is possible to estimate the heat release dq/dt_0 at any temperature T_0:

$$\dot{q}_0 = \dot{q}_{onset} \cdot \exp\left(\frac{E}{R}\left(\frac{1}{T_{onset}} - \frac{1}{T_0}\right)\right) \tag{5.1}$$

With the resulting value for the heat release rate and the estimated value of the activation temperature, the TMR can be calculated. Following Keller again [Keller], the temperature where the TMR is equivalent to 24h can then be estimated with the help of a function of T_{onset}:

$$T_{0,24}[K] = 0.65 \cdot T_{onset}[K] + 50 \tag{5.2}$$

Keller operated with the dynamical measurements at 3K/min and 4K/min. The onset temperatures for the performed experiments at 2.5K/min and 5K/min are both approximately the same with T_{onset} = 85°C. With this onset temperature the temperature where the TMR is equivalent to 24h was calculated to 9.6°C. In the following table 5.1. all results from the DSC are presented. It shows that the most conservative safety limit of 5°C was analysed with the 100K-rule. It is the strictest safety limit and therefore the 5°C are adopted as the safety limit for the decomposition of the hydroperoxide. It is well possible that the

hydroperoxide can also be safely handled at temperatures between 15°C and 20°C, as the maximum temperature according to the TMR of 24h measured with isothermal measurements ended in a value of 39°C. But this has to be proven first with further tests.

Table 5.1: Results from the DSC for the hydroperoxide

Method	maximum Temperature [°C]
100K-rule	5
TMR with isothermal measurements	39
$T_{0,24}$ with dynamical measurements	9.6

With the knowledge of the heat capacity of the sample and the specific enthalpy of the decomposition $\Delta_R h$ [J/mole] the adiabatic temperature rise for the decomposition can be calculated. The value of 208J/(mole·K) for the heat capacity of the hydroperoxide was estimated with the help of two experiments in the DSC. As many organic liquids show similar heat capacities [Perry], the value seems reasonable. The adiabatic temperature rise for the decomposition is as follows:

$$\Delta T_{ad} = \frac{-\Delta_R h}{c_p} = \frac{172800 \frac{J}{mole}}{208 \frac{J}{mole \cdot K}} = 829.5K \tag{5.3}$$

The resulting adiabatic temperature rise of 829.5K for the decomposition of the hydroperoxide is a very high value with a high risk potential, which also indicates, that several precautions have to be taken to run the process.

Further, the formal kinetics for the decomposition was determined with the help of the isothermal tests.

The concentration depends on the reaction rate as follows:

$$\frac{dc_i}{dt} = \nu_i \cdot r \tag{5.4}$$

For a reaction with first order kinetics the reaction rate is defined as:

$$r = k \cdot c_a \tag{5.5}$$

Replacing r and an integration gives:

$$\ln c_a - \ln c_{a0} = \nu_a \cdot k \cdot t \tag{5.6}$$

This result of a linear equation of first order must now be proven with the measured data, which should result in a straight line by showing $\ln c_a$ over t. The time and the heat release rate and therefore the thermal conversion were of course measured continuously by the DSC, but not the concentration. This can be calculated with the help of the thermal conversion. The thermal conversion is defined as follows:

$$X = \frac{\int_0^{\dot{}} \dot{Q} dt}{\int_0^{\infty} \dot{Q} dt} \tag{5.7}$$

Now the concentration can be calculated as follows: $c_a = c_{a0}(1-X)$. These resulting concentration data must in fact be regarded as thermal data, as they are deduced from the thermal conversion. It must be emphasized here that the assumption, the analytical is equivalent to the thermal conversion, is only valid for simple reactions, where only one reaction takes place. In the presented case the decomposition of the hydroperoxide might be of a more complex kinetics due to the catalytic effects of the steel. This catalytic effect is neglected here to analyse if the decomposition can be approximated with a first order kinetics. In the following figure 5.2 an example is shown for calculation of the measured data at 140°C.

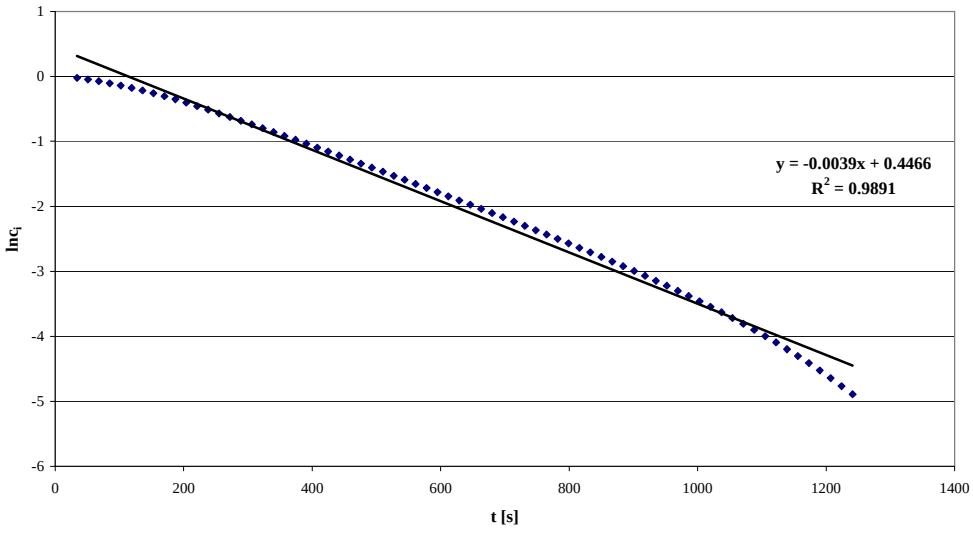


Figure 5.2: Prove for first order kinetics at isothermal test at 140°C

It can be well seen in the figure above, that the reaction is of approximately first order. But it also shows that a first order kinetic is only an approximation. Due to the catalytic effect of the steel test cells, the formal kinetics could be more complex. In another attempt to determine the formal kinetics the differentiation method was used. The decreasing amount of hydroperoxide can be described as follows without giving already the reaction order:

$$\frac{dc_a}{dt} = \nu_a \cdot k \cdot c_a^n \tag{5.8}$$

with n as the reaction order. The equation is now logarithmised and with the help of a diagram the order n can be determined.

$$\ln\frac{dc_a}{dt} = \ln(\nu_a \cdot k) + n \cdot \ln c_a \tag{5.9}$$

The result can be seen in the following figure below.

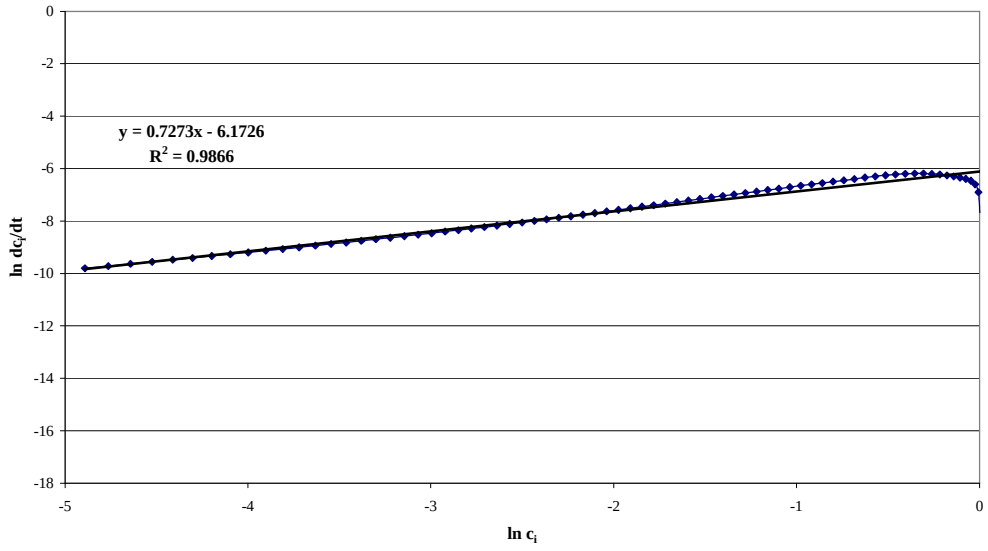


Figure 5.3: Determination of reaction kinetics by differentiation at T_{iso} = 140°C

The diagram 5.3 shows that the decomposition is described even better with a reaction order of 0.73. This is of course a very theoretical order and it always has to be kept in mind that the steel of the sample cells has a catalytic effect.

Furthermore with the resulting data from the isothermal temperatures of 140°C, 145°C and 150°C, the activation temperature can be calculated in a different way. As for all differentiations at the three different temperatures a ln(k) can be determined (as the ν_a is assumed to

be -1, it can be neglected), the activation temperature can be determined with the help of an Arrhenius diagram, showing the ln (k) over the reverse value of the temperature. The activation temperature is then equivalent to the slope and could be calculated to $1.28 \cdot 10^4$ K as can be observed in the following figure.

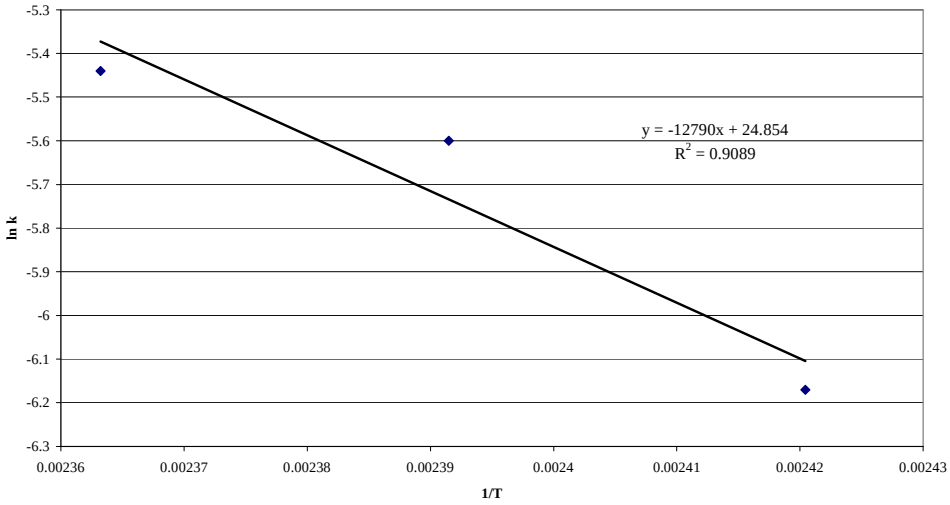


Figure 5.4: Determination of E/R with the differentiation method

The determined value for the activation temperature of $1.28 \cdot 10^4$K correspond very well with the already determined value of $1.28 \cdot 10^4$K, which was calculated directly from the isothermal experiments. But it has to be kept in mind, that both activation temperatures were determined with the same experimental data. Although the figure 5.4 approves the already determined activation temperature, a prove with independent measured data would be necessary to be able to rely completely on this activation temperature of approximately $1.28 \cdot 10^4$ K. Before a detailed interpretation of all results will be given, further experiments in the TEVT and the TSU are presented in the following.

After the analysis in the DSC, the hydroperoxide was also analysed in the TEVT to evaluate the risk of explosibility of the peroxide. Two different types of experiments were performed here. The hydroperoxide was analysed in its pure form and in mixture with the catalyst to test its influence. As already mentioned in chapter 4.1.2 the TEVT was operated in dynamic mode at 18K/min. The temperature of the sample itself as well as the temperature of the gas above are measured. These two measurements are important as usually the explosions start in the gas phase.

The maximum pressure measured in a test of 5g pure hydroperoxide was 4.947MPa (49.47bar). The maximum rise in pressure was 6.52MPa/s and the effect pressure value could therefore be calculated to 32.25MPa²/s. The TEVT had been a UN-test to determine classification and package group for the purpose of hazardous goods. It is usually said that for a pressure effect value of below 10 MPa²/s there is a low risk, values of 10 - 100MPa²/s are regarded as medium and values of 100 to 1000 MPa²/s are taken as violent, finally higher than 1000 MPa²/s as very violent [Nations 1]. Adopting the evaluation proposed in these former guidelines it can be seen, that the pure hydroperoxide carries a medium risk.

In the following figure 5.5 the resulting temperature curve for the experiment with 5g of hydroperoxide is presented.

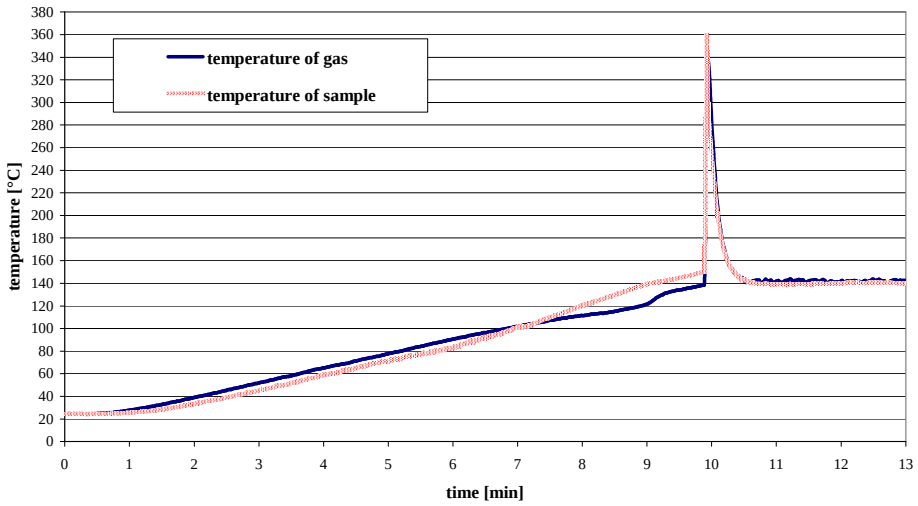


Figure 5.5: Temperature curve from 5g hydroperoxide in the TEVT, max p 49.5bar

To analyse the influence of the catalyst on the decomposition of the hydroperoxide, apart from experiments with the hydroperoxide in pure form, also tests with the hydroperoxide mixed with the catalyst were performed. The results of two typical tests are summarized in table 5.2

Table 5.2: Measurements with hydroperoxide and hydroperoxide mixed with catalyst in the TEVT

Sample	max. pressure	T_{onset} sample	T_{max} sample	T_{onset} gas	T_{max} gas
5g hydroperoxide	49.5 bar	150°C	356°C	138°C	339°C
3g hydroperoxide + 2g catalyst	0 bar	70°C	146°C	52°C	119°C

The result for the mixture with catalyst was reproduced in all tests with the catalyst: a rise in pressure was never detected. In the following figure 5.6 the resulting temperature curve for the experiment with 3g hydroperoxide and 2g of catalyst is shown.

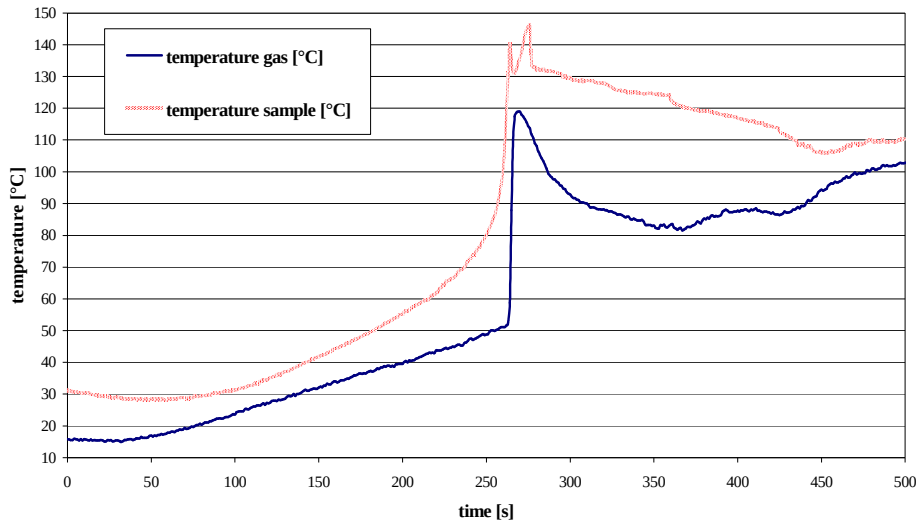


Figure 5.6: Temperature curve from 3g hydroperoxide and 2g catalyst in the TEVT, no pressure detected

The fact, that during the experiment 3g hydroperoxide and 2g catalyst no pressure curve was detected, might be due to the totally lower amount of hydroperoxide, 5g in the tests with hydroperoxide and only 3g in the tests with hydroperoxide and catalyst. The experiments showed further that the onset as well as the maximum temperatures in the gas phase are lower than in the sample. The onset and maximum temperatures measured in the TEVT are not as reliable as in the DSC, but are interesting in comparison to the test hydroperoxide mixed with catalyst. The experiments show that the catalyst lowers the onset temperature for the decomposition significantly for more than 70°C. This will have a great influence on the process.

A further test was performed in the TS^U to verify the pressure results. A sample cell was filled with 3.6g hydroperoxide and a ramped test with 5K/min performed as can be seen in the following figure 5.7. The maximum pressure measured was 29bar, but as the test cell ruptured it might have been higher. It is assumed that the steel test cell has a catalytic effect on the hydroperoxide and this caused the high pressure and the rupture of the test cell. Also a glass test cell was used for an experiment in the TS^U, but the pressure could not be meas-

ured either, again due to a rupture of the test cell. It is assumed that already the metallic Pt100 used to measure the temperature inside the sample causes the catalytic effect and the rupture of the test cell.

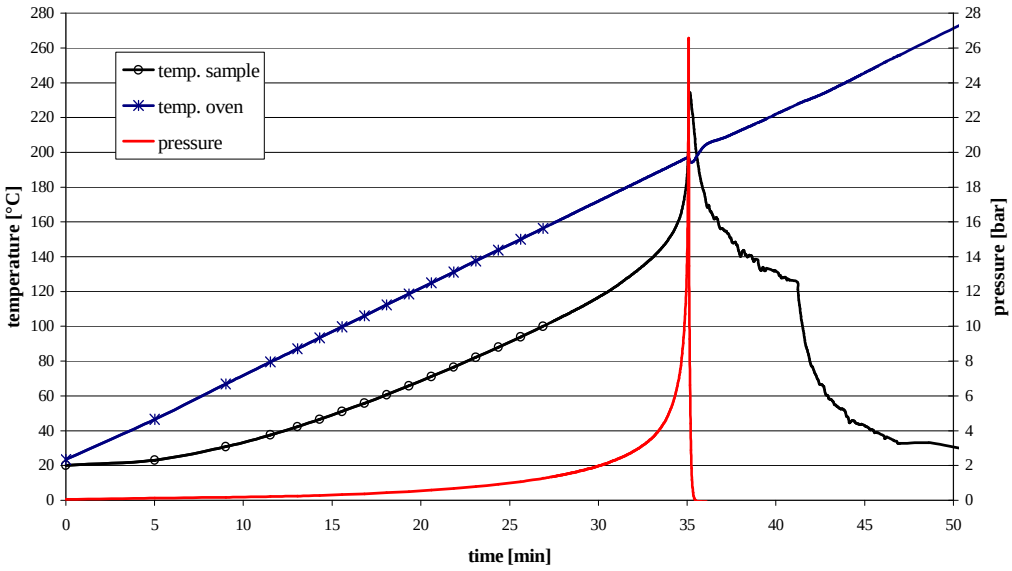


Figure 5.7: Test with 3.6g hydroperoxide in the TS^U

According to the measurements of the rise in pressure with increasing temperature it can be stated for the hydroperoxide, that no maximum pressure could be detected with the TS^U.

The last pressure measured in the TS^U of 29bar leads to the assumption that the measured maximum pressure in the TEVT of 49.5bar is a reasonable value. Furthermore it is assumed that even in the TEVT with its glass test cell a catalytic effect has to be taken into account, as it was also operated with a metallic Pt100, which plunged into the liquid sample. Furthermore the gas phase above the sample had contact with the steel vessel of the TEVT during the experiment.

To summarize all experiments with the hydroperoxide in a recommendation for a safe handling of it, it must first be stated that according to the 100K-rule the temperature should not exceed 5°C. The hydroperoxide has a high decomposition enthalpy of $\Delta_R h$= -172.8kJ/mole, which might indicate a tendency to explosiveness. Tests in the TEVT then showed that this risk can, according to the former UN-guidelines, be regarded as medium, the maximum pressure detected was 49.5bar. Evaluations of the experiments in the DSC showed that its

activation temperature is approximately 12800K. A further result of these evaluations was an approximation of a first order formal kinetics for the decomposition. But all isothermal experiments showed that there might be a catalytic effect on the decomposition by the steel of the sample cells. This catalytic effect enhances the decomposition reaction, and was also found during the experiments in the TEVT and the TS^U. As it was supposed that also the catalyst has a catalytic effect on the decomposition, a mixture of catalyst and hydroperoxide was analysed in the TEVT. It proved the assumption, the catalyst lowered the onset temperature significantly.

It can be concluded that for a safe handling of the hydroperoxide, the temperature should not be higher than 5°C and any catalytic effects by steel or the catalyst should be avoided.

5.1.3. The solid

Like the hydroperoxide, the solid was first tested in the DSC. The substance did not show a decomposition until 300°C. It melted at 138°C. Therefore no thermal runaway has to be expected from it. It was not analysed further.

5.1.4. The di-peroxide

Like the hydroperoxide, the di-peroxide was first analysed in the DSC and it was started with dynamical tests at heating rates of 1K/min; 2.5K/min; 5K/min and 10K/min. Results can be observed in the following figure 5.8. Again the 100K-rule was applied and gave a first safety limit of 32°C maximum temperature. The temperature shift was in normal range, as the gradient of dln(HR)/dt was with 0.0852 greater than 0.057 and the 100K-rule could therefore be applied. The average decomposition enthalpy of the four tests at different heating rates was $\Delta_R h$=-273.2kJ/mole.

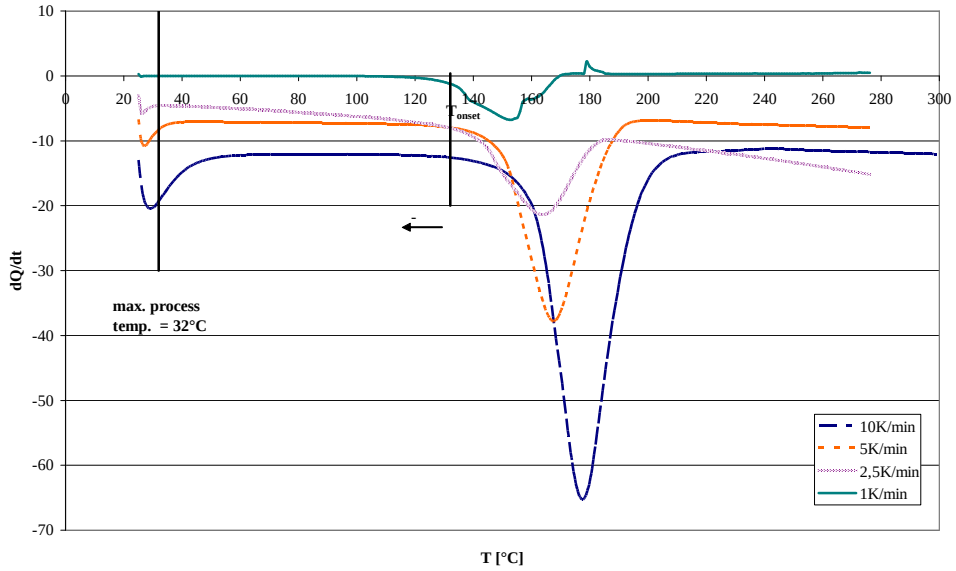


Figure 5.8: Dynamical tests of the diperoxide

The dynamical tests were followed by isothermal tests at temperatures of 150°C, 155°C and 160°C. In the following figure 5.9 the determination of the activation temperature of the di-peroxide can be seen.

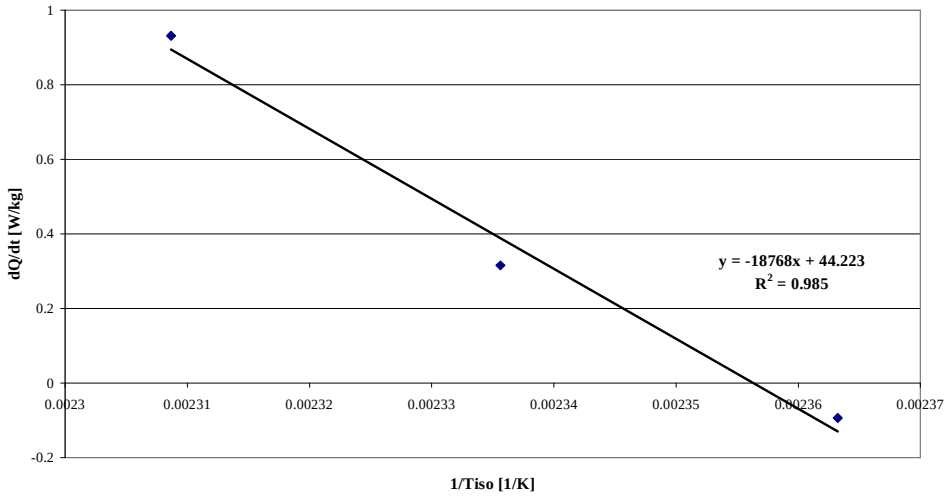


Figure 5.9: Determination of the activation temperature of the di-peroxide

The activation temperature of the di-peroxide was determined to $1.88 \cdot 10^4$ K and the TMR for a temperature of 150°C was therefore calculated to 3.1s (for the isothermal temperature of 155°C the isothermal temperature was calculated to 2.1s and for 160°C to 1.2s). As in case for the di-peroxide the isothermal method for the determination of the activation tem-

perature worked well, no other methods as for the hydroperoxide were used. As the process is planned to be operated not at 150°C but at lower temperatures, the temperature for a TMR of 24h had to be calculated. This calculation can be made with the help of the plot ln(TMR) versus 1/Tiso, which again gives a straight line and therefore an estimation for all values of TMR or isothermal temperature. The plot for the values of the di-peroxide can be seen in the following figure 5.10.

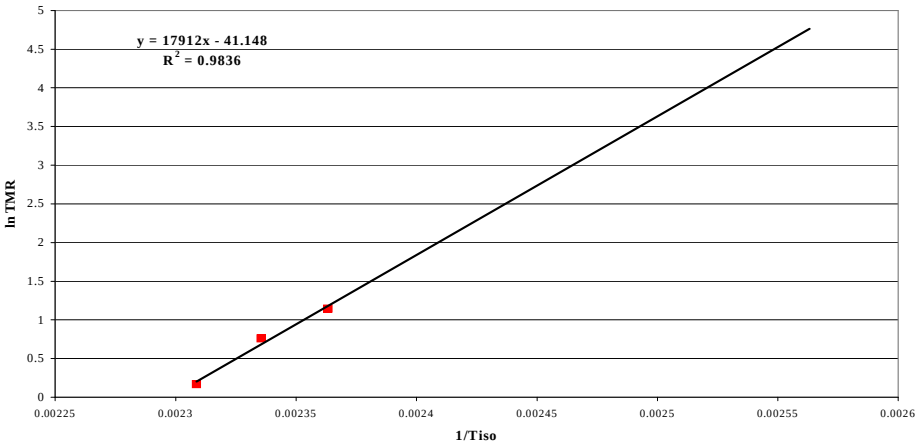


Figure 5.10: Determination of TMR at different temperatures for the di-peroxide

For a safe process usually a TMR of 24h is preferred. The corresponding temperature for a TMR of 24h for the di-peroxide was calculated to 68°C. This is a lot higher than the planned process temperature, which means that the di-peroxide is not expected to require extra pre-cautions. With another approximation of the heat capacity of the di-peroxide to 545J/(mole·K) and the specific enthalpy of the decomposition $\Delta_R h$ [J/mole] of -273.2kJ/mole the adiabatic temperature rise for the decomposition can be calculated to 500K. Similar to the hydroperoxide this is an adiabatic temperature rise with a very high risk potential.

As for the hydroperoxide the isothermal tests were also evaluated in order to determine reaction kinetics. Due to these evaluations the decomposition of the di-peroxide can also be approximated with a first order kinetics, like the hydroperoxide. But similar to the results of the hydroperoxide, with a first order kinetics, the catalytic effect of the steel of the test cells is neglected. Applying the differential method, an order of 0.68 is found, which fits even better. The corresponding figures can be observed in the appendix A.1.

The di-peroxide was then analysed in the TEVT for the evaluation of the rise in pressure. The tests of 5g di-peroxide did not show a high maximum pressure, the maximum pressure measured was 20.7bar, the maximum rise in pressure was 8.83MPa/s and the effect pressure value could therefore be calculated to 18.28MPa²/s. The corresponding figures are found in the appendix A.2. According to the former UN-guidelines this is regarded as medium risk.

Concerning the safety the di-peroxide has a high hazard potential due to an exothermic decomposition enthalpy of $\Delta_R h$ = -273.2kJ/mole. Further experiments in the TEVT showed a medium risk according to its explosiveness and a maximum pressure of 20.7bar. No strong catalytic effects of the steel of the DSC test cells were found. Isothermal DSC measurements and the determination of the activation temperature of $1.88 \cdot 10^4$K as well as the temperature for TMR of 24h of 68°C worked well. The maximum temperature according to the 100K-rule was calculated to 32°C and is recommended as a safety limit as it is the most conservative limit.

5.1.5 The intermediate

The intermediate was mainly produced in the diluted experiments in the RC1*e* which are described in chapter 5.2. As the hazard potential for this substance was not known either, it was as well analysed in the DSC and the TEVT. It was not isolated and therefore always analysed in mixture with the di-peroxide and the hydroperoxide. The concentrations were analysed in the HPLC. As the intermediate did not exist in pure form, its concentration in the sample could only be estimated. The configuration was as follows: 49.5 weight% hydroperoxide, 21 weight% di-peroxide and 29.5 weight% intermediate (estimated).

Again it was started with dynamical tests in the DSC. The average decomposition enthalpy in the dynamical tests was -1323.6J/g. The possibility of applying the 100K-rule was checked, the gradient dln(HR)/dT was 0.0757 >0.057 and the 100K-rule could therefore be applied and the temperature programmed curves for the determination of the maximum temperature can be observed in the following figure 5.11.

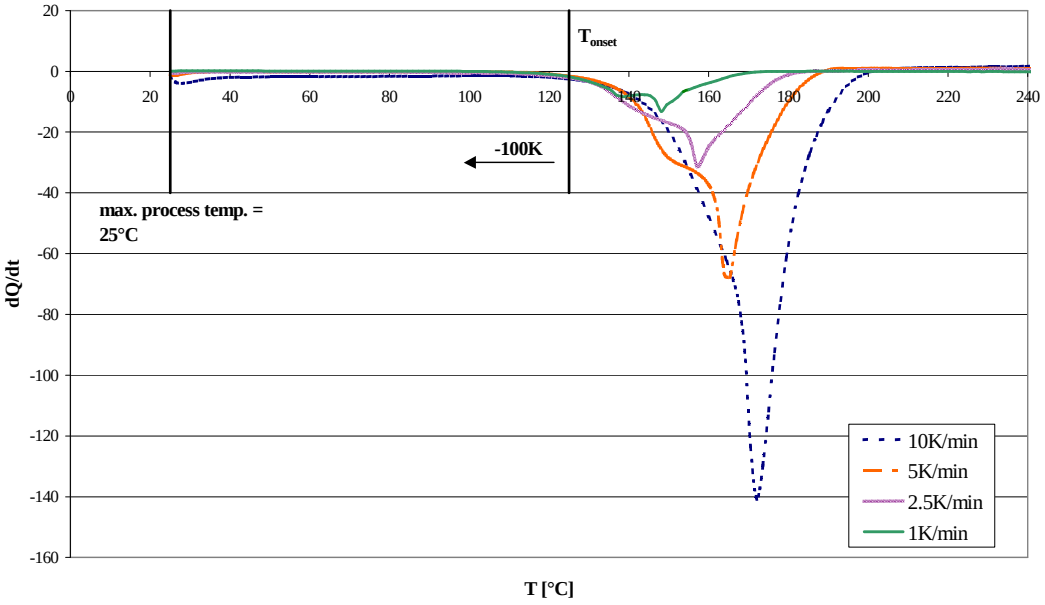


Figure 5.11: Dynamical tests of the intermediate

The onset temperature of the test at 10K/min was 125°C and the maximum tolerable temperature due to the 100K-rule is therefore 25°C.

Isothermal tests were performed at 145°C, 150°C, 155°C and 160°C. The activation temperature E/R was then calculated to 9356.8K and the time to maximum rate (TMR) for a process temperature of 15°C was determined to approximately 66h. At a temperature of 25.2°C the TMR would be equivalent to 24h. Furthermore the decomposition of the intermediate could also be approximated with a first order kinetics scheme. The differential method was not applied this time, as the intermediate could not be measured in pure form and an approximation of the reaction order would therefore be sufficient. All figures can be found in the appendix A.1.

Finally the rise in pressure was analysed in the TEVT. The tests of 5g intermediate showed a maximum pressure of 25.1 bar or 2.51 MPa. The maximum rise in pressure was 14.4 MPa/s and the effect pressure value could therefore be calculated to 36.2 MPa^2/s, see also appendix A.2. According to the former UN-guidelines this is regarded as medium risk.

For a recommendation for a safe handling of the intermediate all results from the DSC and the TEVT are regarded. The intermediate, like the hydroperoxide and the di-peroxide, has a high hazard potential due to exothermic decomposition enthalpy of $\Delta_R h$ = -1320J/g. Experiments in the TEVT showed a medium risk according to its explosiveness and a maximum pressure of 25.1bar. Isothermal DSC measurements and the determination of the activation temperature of 9357K as well as the temperature for TMR of 24h of 25.2°C worked well. The maximum temperature according to the 100K-rule was calculated to 25°C and is therefore recommended as a safety limit.

5.1.6 Recommendations on a safe handling of the substances in pure form

From the four analysed substances, the three peroxides, hydroperoxide, di-peroxide and the intermediate have a high hazard potential, while the solid did not show any exothermic reaction during the DSC measurement. It is therefore regarded as safe and not discussed any more.

In the following table 5.3 the main results of the three analysed substances, intermediate, di-peroxide and hydroperoxide are summarized.

Table 5.3: Results of the analyses of the reactants in pure form

Substance	max T according to 100K-rule [°C]	T for a TMR of 24h [°C] (isothermal measurements)	max p [bar]	Δrh [kJ/mole]
hydroperoxide	5	39	49.5	-172.8
di-peroxide	32	68	20.7	-273.2
intermediate	25	25	25.1	-1320 [J/g]

The determined parameters in table 5.3 clearly show that the hydroperoxide has the highest risk potential. Compared to it the di-peroxide seems to be well controllable with a maximum temperature according to the 100K-rule of 32°C and a decomposition enthalpy of $\Delta_R h$ = -273.2kJ/mole, while the intermediate with a maximum temperature according to the 100K-rule of 25°C and a decomposition enthalpy of $\Delta_R h$ = -1320J/g lies in between those two. This could be expected, as the intermediate is, as its name already says, a precursor on the way to the di-peroxide. Evaluations of isothermal DSC experiments showed that for all three substances the decomposition reaction can approximately be described with a first

order formal kinetics. The isothermal DSC experiments for the intermediate and the di-peroxide could be performed without problems, but not for the hydroperoxide. Obviously the steel of the sample cells had a catalytic effect on the decomposition. This effect was also found during the experiments in the TEVT and the TS^U. It was therefore also tested if the catalyst has a catalytic effect on the decomposition reaction, too. The experiments in the TEVT showed that the onset temperature was significantly lowered by the catalyst.

All peroxides showed a rise in pressure during the experiments in the TEVT with the highest value of 49.5bar from the hydroperoxide. Concerning their explosiveness they all carry a medium risk according to the United Nations Orange Book [Nations 1].

Out of these safety criteria with 5°C the most conservative value is adopted as a safety limit, as the hydroperoxide carries the highest risk potential. For a safe handling of all substances the temperature should be kept under 5°C. The contact of the hydroperoxide with steel and the catalyst should also be avoided, as these have catalytic effects on its decomposition reaction and can lower its onset temperature. Concerning the catalytic effect of steel, this is already considered in the maximum temperature of 5°C, as it was determined with steel test cells. But the catalytic effect of the catalyst was not considered and therefore a contamination of the hydroperoxide with it should absolutely be avoided.

5.2. Analysis of the synthesis reaction

After the analysis of the substances in pure form in chapter 5.1, the synthesis reaction has to be analysed. The experiments were performed first in a 250ml laboratory reactor under different conditions and then in the RC1*e*. After a short introduction to the related problems, the experiments and their results will be shown. The chapter 5.2 will close with a conclusion.

5.2.1 Introduction

In general the analysis of the process should start on small scale to lower the hazard potential. First the process parameters and their deviations like addition time and reaction temperature have to be analysed. If these first experiments on small scale were successful and the reaction is good controllable, the next scale can be started.

In the last chapter 5.1 the substances were analysed in pure form and it was found that they have a great hazard potential. For a safe handling of the substances according to the 100K-rule the temperature should not exceed 5°C. If the process is operated at higher temperatures than 5°C, the experiments have to be carried out in a very careful way. It was started with a small laboratory reactor of 250ml, where first process parameters were analysed. The changing addition time and changing ratio of the hydroperoxide as well as an analysis of the influence of the particle size on the synthesis reaction were performed on this small scale. After the successful performance of these experiments, a larger scale of 1l in the RC1*e* was tested. Experiments were performed in the RC1*e* to detect the reaction kinetics and finally tests were run in a diluted system in order to achieve safety.

5.2.2. Analysis of reaction parameters

As already mentioned in the introduction, before starting to analyse the synthesis reaction on 1l scale, important process parameters should first be analysed in small scale. In the presented case the 250ml laboratory reactor was used. It was operated as a semi-batch reactor in an isoperibolic mode. The reaction was started with the addition of the catalyst. Many

experiments were performed at the planned process temperature of 15°C. As for the semi-batch reactor the released heat can be controlled by the addition, the temperature of the reactor should not rise but stay close and stable to the planned process temperature.

The first parameter analysed in order to achieve a safer system was the addition time of the catalyst. In the following figure 5.12 it is shown that the addition time for the catalyst should not be too short. All three experiments were performed at equal conditions, 500rpm stirring, 12-14°C start temperature, same amount of substances.

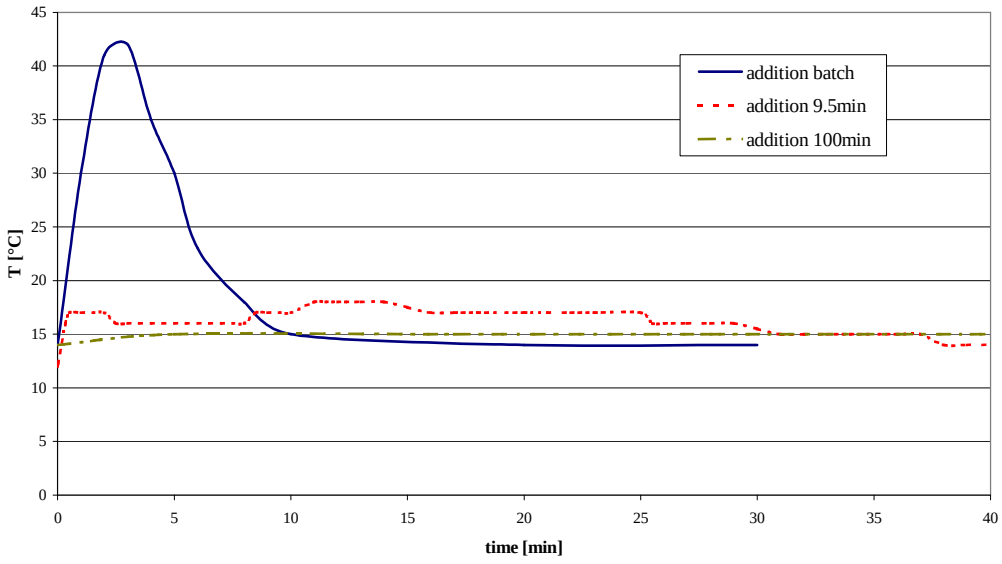


Figure 5.12: Different addition time of catalyst

It can be well observed, that the instantaneous addition, where the conditions are equivalent to a batch-reactor, followed a steep rise in temperature up to over 40°C. The addition within 9.5min still ended up in a rise in temperature up to 18°C. Only the addition of over 100min showed the normal and desired behaviour and stayed very stable at 15°C

The experiment with the immediate addition of all catalyst, the batch experiment, showed that the reaction is instantaneous. As in this case an addition controlled reaction is favoured, for the following experiments the catalyst was always added within 30min.

Another analysed parameter was the ratio of solid to hydroperoxide. The aim was to determine the optimal ratio of solid to hydroperoxide. In the following figure 5.13 two experiments are shown, one with the hydroperoxide in great excess and one close to the

stoichiometric point with the solid (n_A) as the limiting component. All other conditions were kept equal. The stoichiometric input ratio can be calculated for the first case, hydroperoxide (n_B) in excess:

$$\lambda = \frac{-\nu_B}{-\nu_A} \cdot \frac{n_{A,0}}{n_{B,0}} = \frac{2}{1} \cdot \frac{0.026\text{mole}}{0.23\text{mole}} = 0.226 \tag{5.10}$$

For the second case, with the ratio closer to the stoichiometric point:

$$\lambda = \frac{-\nu_B}{-\nu_A} \cdot \frac{n_{A,0}}{n_{B,0}} = \frac{2}{1} \cdot \frac{0.093\text{mole}}{0.23\text{mole}} = 0.81 \tag{5.11}$$

In the first case there is approximately five times more hydroperoxide in the solution than needed for the reaction while in the second case there is only a slight excess.

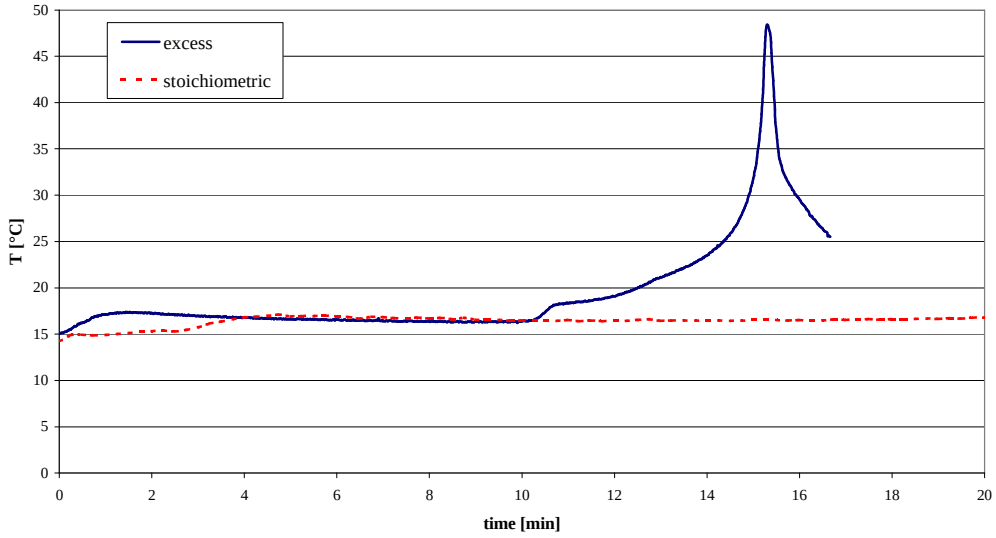


Figure 5.13: Different ratio of hydro-peroxide/solid

As can be seen from figure 5.13, the experiment close to the stoichiometric point has a stable temperature curve while the experiment with the hydroperoxide in great excess ends up in a runaway. After these tests the synthesis was always performed close to the stoichiometric point as tests ended up in a runaway various times when performed with great excess of hydroperoxide. This might be due to the catalyst, which lowers the onset-temperature for the decomposition of the hydroperoxide (see chapter 5.1.2.). The hydroperoxide in excess reacts with the added catalyst and the decomposition starts, which is highly exothermic, the temperature cannot be controlled any more and a runaway occurs.

5.2.3. Influence of the particle size

As already mentioned in chapter 2.1 the solid cannot be specified further, because company secrets have to be respected. But it is known that the solid exists in meta and para isomers.

Two different types of solid were used, one very heterogeneous in particle size and only of 88% content, a mixture of meta and para isomers, further named solid I. The second type had 99% content, was of smaller size and consisted of mainly para isomers, further named solid II.

To analyse the influence of the particle size of the two types, both were first sieved and separated into different fractions. In the following figure 5.14 the particle size distribution of the solid I and the solid II can be observed.

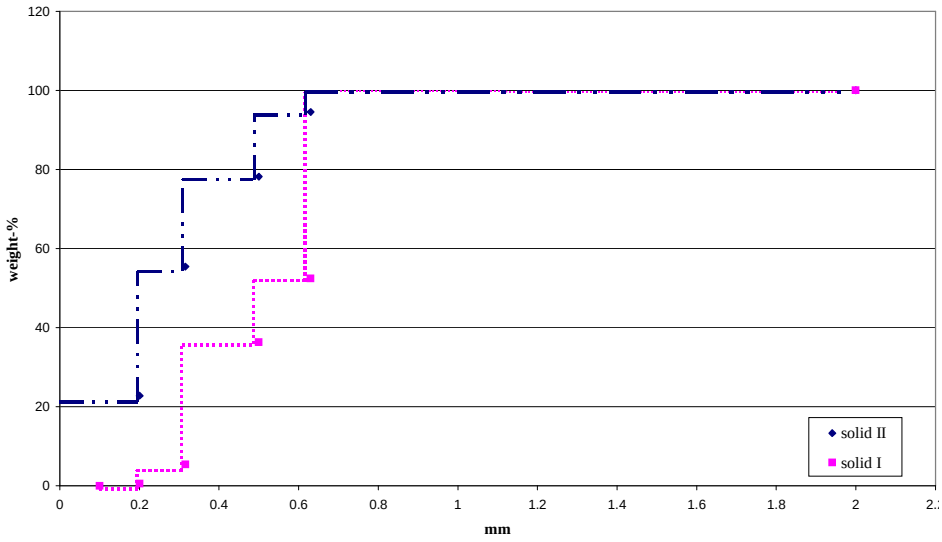


Figure 5.14: Particle size distribution of solid I and solid II

It can be observed in figure 5.14 that over 90% of the solid II is smaller than 0.63mm while a large amount (almost 50%) of solid I is larger than 0.63mm.

For a better characterisation of the particles of the solids, aggrandised pictures were taken with a raster electronic microscope (Hitachi, S2700). These photos can be seen in the following two figures 5.15 and 5.16. They show that the „particles“ themselves are all agglomerates of very small particles. After a rough estimation from the second photo, the small particles are approximately 60µm long and 5µm wide, sticking together they give an agglomerate or visible „particle“.

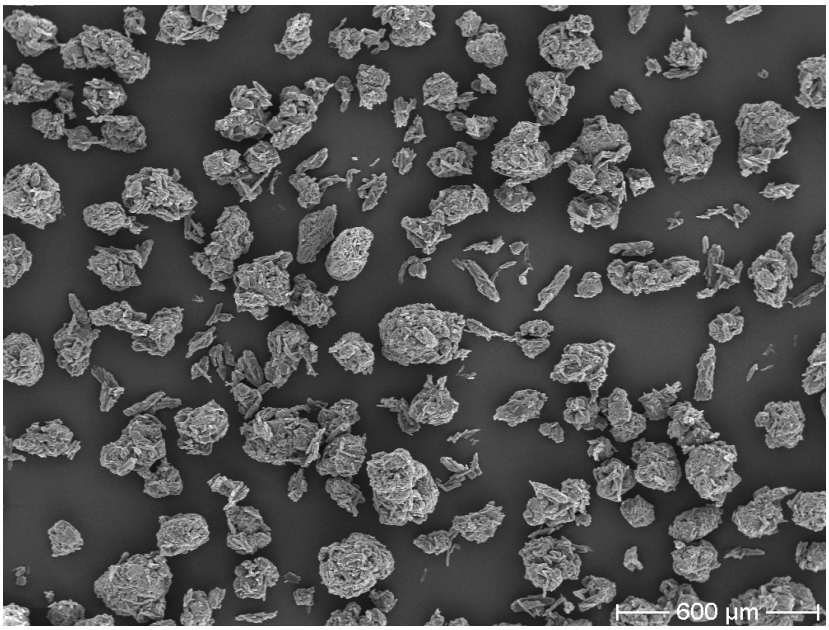


Figure 5.15: Photo of the solid, various „particles“, solid I, fraction <0.1mm

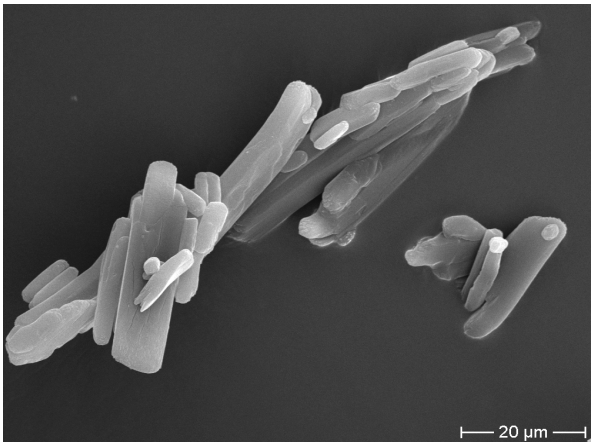


Figure 5.16: Photo of one „particle“ of the solid I, fraction <0.1mm

For the characterisation of a possible influence of the particle size on the reaction experiments were performed with the different fractions. In the following table 5.4 the different fractions are shown.

Table 5.4: Fraction sizes of the sieved solid

Fraction size
<0.1mm
<0.2mm
<0.315mm
<0.5mm
<0.63mm
>0.63mm

The experiments were performed in the mini-laboratory reactor. A test series was started with 20g of the solid to 28g of hydroperoxide to avoid a too great excess of it and therefore its decomposition, 1.5g water and 43g catalyst. The resulting temperature curves can be seen in the following diagram figure 5.17.

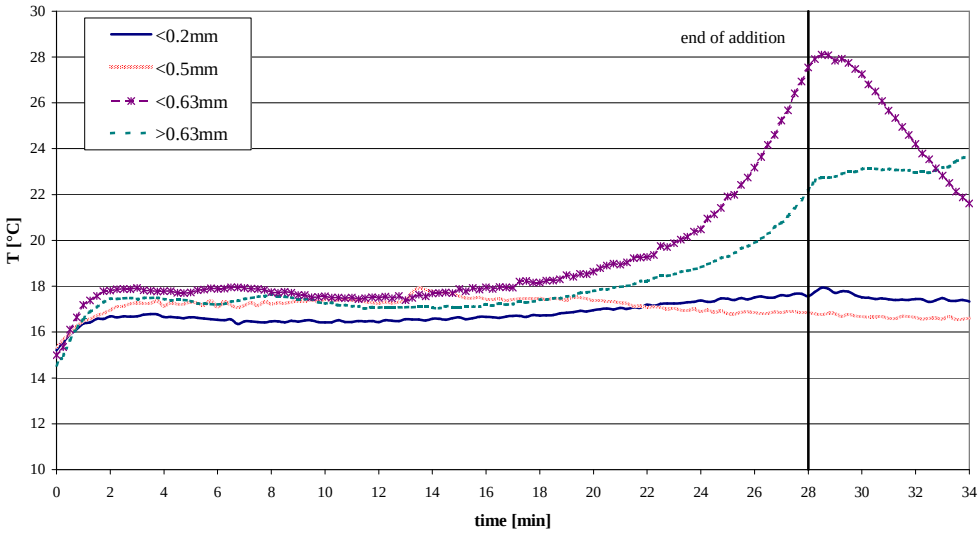


Figure 5.17: Temperature curves of tests with different particle sizes

It must be stated that the experiments did not show the anticipated results. It was expected that the smallest fraction shows the highest potential of a runaway, due to the highest relative surface area. But, unexpectedly, the smallest fraction did not show any sign of a runaway, instead the temperature stayed relatively stable at around 17°C during the reaction. In

contrast, the fractions with the larger particle size, fraction <0.63mm and >0.63mm, seemed more to have the tendency of a thermal runaway. It was concluded that the particle size somehow had an influence, but not the expected one.

For a closer analysis of the influence of the particle size, it had to be known first, where the reaction takes place. It could take place in the film around the solid and would then be controlled by the relative surface area of the solid. Or, it could take place in the liquid and would then be controlled by the solubility of the solid in the hydroperoxide. Therefore tests on the solubility of the solid were performed. It was tested if the solid was soluble in water, in the catalyst and in the hydroperoxide. It turned out not to be soluble in water neither in the catalyst. Very few solid is soluble in the hydroperoxide, with the help of the HPLC a maximum value of 8g solid in 1000g hydroperoxide was measured. Therefore it might well be possible that the reaction takes place in the film around the solid and that the dissolution of the solid in the hydroperoxide only has a minor influence on the reaction.

Following this it can be assumed now that the reaction takes place in the film around the solid particles. Two theories will be presented to explain the differing temperature curves with different particle sizes.

As was discovered from the photos in the raster electronic microscope, the solid (type I) consisted of small crystals, which were agglomerated. Keeping in mind this agglomeration, which of course occur more frequently and in greater sizes in the "bigger" fractions, the resulting peaks in the temperature curves might be due to a „breaking“ of these agglomerates. The resulting smaller pieces then offer a greater surface area for the reaction and cause a rise in temperature due to an increasing reaction rate.

To support this first theory, it was tested if the agglomerates can be broken by simple stirring. Two samples of the fraction >0.63mm were taken and one stirred in approximately 100ml of water for 15min, the second one for 30min. Then the samples were dried and sieved again to analyse the changing composition of the particle sizes. It resulted that after 15min stirring 6.3% of the particles were smaller than 0.63mm and after 30min stirring 16% of the particles were smaller than 0.63mm. It resulted that the stirring might be responsible for the crushing of the particles and finally with the offering of a higher particle surface immediately as well for the temperature peaks. On the other hand it must be stated

that a crushing of 16% of the particles within 30min is not a high amount. It can therefore be doubted that the „breaking“ of the particles is alone responsible for the significantly steeper rise in temperature for the curves with larger particle sizes.

The second theory deals again with the catalytic effect of the added catalyst on the decomposition of the hydroperoxide. It can be said, that apart from the dissolving of the solid, there are two competing reactions. The reaction of the solid with the hydroperoxide to the di-peroxide and the decomposition of the hydroperoxide. It seems that if enough reaction partners of the solid and the hydroperoxide are present, the reaction of the solid with the hydroperoxide to the di-peroxide is favoured. In the experiments with the smaller fraction, only a small amount of the hydroperoxide seems to decompose. This might be due to the fact that the relative surface area of the film around the solid is high and enough reaction partner of the solid present. But in the experiments with larger particle sizes, the amount of available solid reaction partners is smaller due to its smaller relative surface area. With the end of the addition there is too much catalyst present, which is not needed for the synthesis reaction and then catalyses the decomposition of the hydroperoxide. This decomposition of the hydroperoxide has a higher reaction enthalpy than the synthesis reaction (see also chapter 5.2.4) and the temperature rises steeply.

After the presentation of the two theories it is assumed, that both described phenomena have an influence on the steep temperature rise for the experiments with larger particles. But as the released heat at the experiments with larger particles is higher than for the smaller particle fractions, it is assumed that the second theory and therefore the decomposition of the hydroperoxide has a much greater influence than a possible „breaking“ of the particles.

For an always safe process it therefore might be the best to use the solid in a very small particle size, to provide it always soluble in the reaction mixture or at least to provide it in a small size and therefore high relative surface, which gives a relatively larger film around the particles. This might help that the synthesis reaction is favoured instead of the decomposition of the hydroperoxide and therefore keeps the temperature and the reaction stable.

5.2.4. Synthesis reaction at different temperatures at 1l-scale

After the successful analysis of the synthesis reaction in the 250ml laboratory reactor, it was operated in the next scale at 1l. The influence of the reaction temperature on the synthesis reaction was analysed.

Therefore experiments were performed in the reaction calorimeter RC1*e* from Mettler Toledo at four different temperatures, 5°C, 10°C, 15°C and 20°C. The amount of substances was equal for all experiments. It was started with 1.09 mole solid and 2.7mole hydroperoxide in the reactor, approximately 3.57mole of catalyst were added within 30min. As 2mole of hydroperoxide and one mole of solid are required to form one mole diperoxide, the hydroperoxide is present in a slight excess (λ=0.8).

All experiments showed a strong dependency of the heat production on the addition of the catalyst, with the end of the addition usually the heat production decreased rapidly. Only the experiment at 20°C showed a different behaviour, which will be explained later. This strong heat production and its decrease with the end of the addition might not only be caused by the reaction itself but also be due to the dissolution heat of the catalyst. This dissolution heat of the catalyst is for an infinite dilution in water equivalent to -95.28kJ/mole [Atkins]. As 3.57mole of catalyst are added this would give a total released heat of -340kJ for an experiment. The total released heat for each experiment is lower, and as the catalyst is not diluted infinitely and furthermore used for the synthesis reaction, it is supposed, that the dissolution has a minor effect, but still might explain the immediate and strong decrease of the heat release rate with the end of the addition. The dissolution heat of the catalyst in the hydroperoxide without the solid and therefore the synthesis reaction could not be tested. It was tried with the 250ml laboratory reactor, but as was already mentioned in earlier chapters, the catalyst catalyses the decomposition of the hydroperoxide. The experiment ended in a thermal runaway due to the decomposition of the hydroperoxide.

During all experiments various samples were taken to analyse the production of the di-peroxide in the HPLC as well. With the help of these samples the analytical conversion was calculated.

In the following figure 5.18 the diagram for the experiment at 10°C is shown.

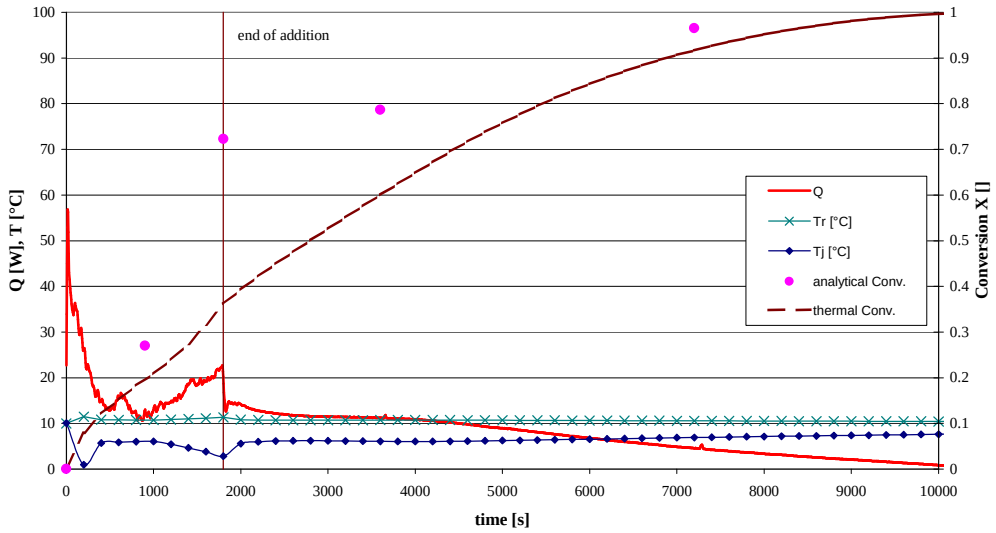


Figure 5.18: Synthesis at 10°C in the RC1*e*

It can be seen from the diagram that most of the di-peroxide was produced during the first 30min while the catalyst was added. In this experiment the analytical conversion at the end of the addition was approximately 72% and at the end of the experiment 96%. As described in chapter 2.1, out of one mole solid one mole di-peroxide is formed. For the analytical conversion the amount of produced di-peroxide was therefore referred to the amount of solid at the start of the reaction. The calculation was as follows: $X = n_{di\text{-}peroxide}/n_{0,\,solid}$ with the help of the amount of produced di-peroxide, which was analysed in the HPLC.

From the figure 5.18 it can be further seen that the heat release rate has its highest point with the beginning of the addition of the catalyst and it decreases rapidly with the end of addition. This is supposed to be due to the dissolution heat of the added catalyst in the liquid, which immediately stops when no more catalyst is added. Therefore from the diagram figure 5.18 it cannot be stated that the system is controlled by the addition. For an addition controlled system the heat release rate should decrease immediately with the end of the addition, while in figure 5.18 there is obviously an accumulation, as the heat release rate decreases very slowly within approximately 2h to zero. Another argument against an addition controlled system is the fact that the thermal conversion is only at 36% with the end of the addition, but 99% at the end of the experiment.

The thermal conversion is not equal to the analytical, which may be due to the dissolution heat on the one hand and to a possible secondary reaction, the decomposition of the hydroperoxide, on the other hand. As the released heat is not exclusively produced by the synthesis reaction, it is not reasonable to work with the thermal conversion. Therefore no more thermal conversion will be presented in the following.

As a second example for the experiments at different reaction temperatures, the experiment at 20°C is shown in the following figure 5.19.

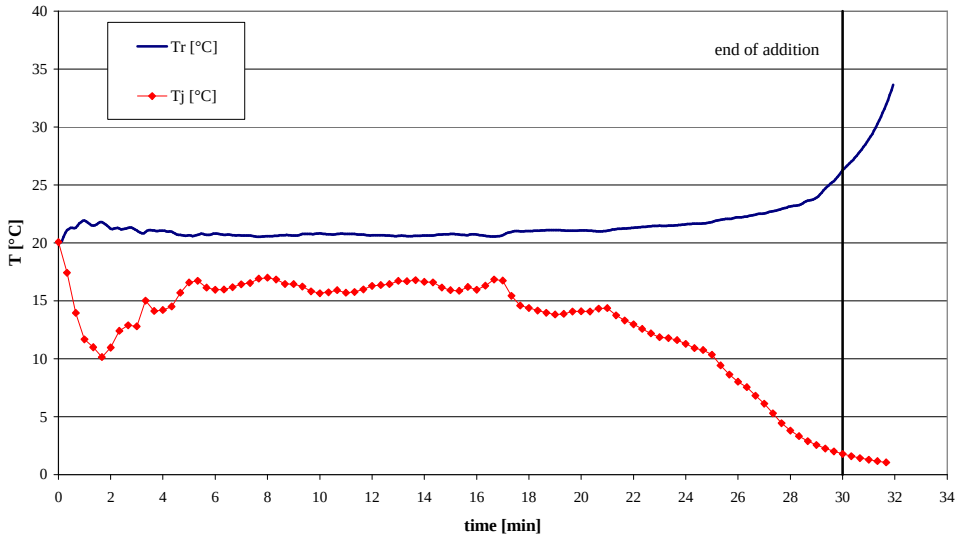


Figure 5.19: Synthesis at 20°C in the RC1*e*

For a better overview, in the figure 5.19 only the temperature of the reactor and of its cooled jacket are shown. This test had to be stopped shortly after the end of the addition of the catalyst, as the temperature started to rise steeply and a thermal runaway was feared. It is assumed that with the higher reaction temperature and a high amount of catalyst, at the end of the addition the decomposition of the hydroperoxide started. Nevertheless two samples were still taken, one during the rise in temperature and a second one after the end of the experiment. The second of these samples showed a lower content of di-peroxide than the first one so that it is assumed that also the decomposition of the di-peroxide had already started. In fact, the di-peroxide was found to be thermally stable up to an onset of 130°C approximately in the tests in the DSC. But, first, this was measured without the catalytic effect of the now added catalyst. Secondly, the temperature of the reaction mixture could have been locally higher than reported. Therefore a decomposition of the di-peroxide

seems possible.

It is further possible that the intermediate started to decompose as well. It had already be shown in chapter 5.1.2. that the catalyst obviously lowers the onset-temperature of the hydroperoxide. It might as well be possible that the onset-temperature of the intermediate is also lowered by the catalyst and therefore a temperature of 20°C is already too high for a safe process.

In the first evaluation of all experiments it was noticed that the reaction enthalpy changed with the isothermal temperature which can be seen in the following table 5.5. All experiments were carried out under equal conditions.

Table 5.5: Reaction enthalpy of different experiments

Isothermal temperature [°C]	Enthalpy/mole solid [kJ/mole]	Enthalpy/mole hydroperoxide [kJ/mole]
5	51.7	20.4
10	84.0	33.1
20	132.1	52.2

Different reaction enthalpies with changing isothermal temperatures are always a sign for a parallel or consecutive reaction. As can be seen in the table 5.5 the reaction enthalpy of the synthesis, referred to mole hydroperoxide, increases with increasing reaction temperature. This is an indication for a parallel or consecutive reaction, which has a higher reaction enthalpy than the synthesis reaction. The decomposition of the hydroperoxide has a very high enthalpy of -172.8kJ/mole. It is therefore assumed that there is a second reaction, the decomposition of a peroxide.

As it could be concluded from the first experiments in the RC1*e* that parallel to the synthesis reaction there is a decomposition reaction of the hydroperoxide, it was tried to quantify this decomposition. With the help of the measurements in the HPLC the amount of di-peroxide and hydroperoxide in the reaction mixture was measured. As it is known that for the formation of one di-peroxide two hydroperoxides are necessary, the theoretical amount of hydroperoxide in the solution can be calculated. The real amount of hydroperoxide in the solution is measured and the difference between those two values can therefore give an indication on how much hydroperoxide decomposed.

In the following figure 5.20 the analytical conversion is shown as well as the theoretical (calculated) and real (measured) amount of the hydroperoxide.

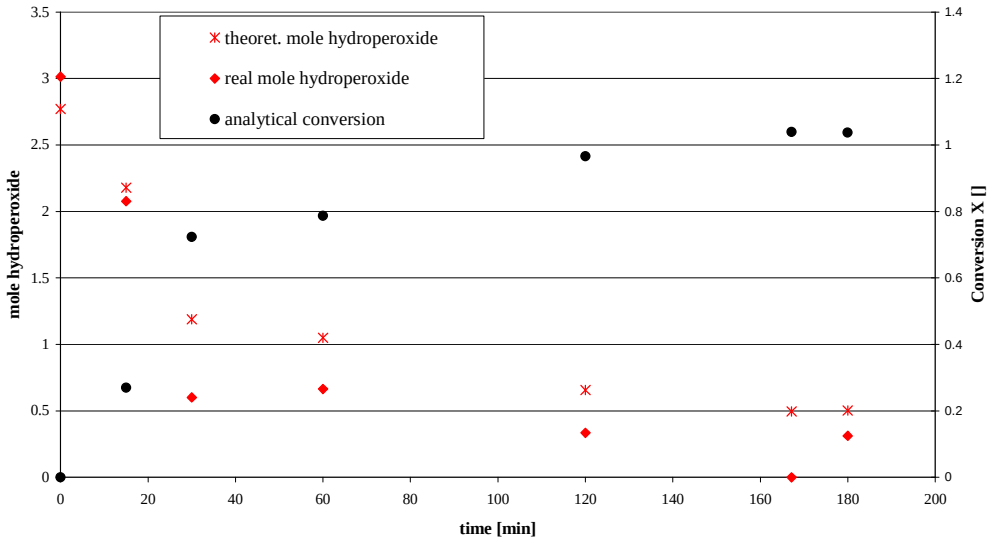


Figure 5.20: Thermal and analytical conversion at 10°C

In the figure 5.20 it can be seen that the theoretical and the measured amount of the hydroperoxide are quite identical at the beginning of the reaction, with small deviations which are obviously due to measuring errors. But after the first 15min of the experiment, the theoretical amount of hydroperoxide is always higher than the measured. Even if measuring errors, for example the unrealistic value of zero hydroperoxide after 165min, but 0.3mole after 180min, are considered, it shows that there is a significant decrease of hydroperoxide which can be referred to the decomposition reaction.

In the following table 5.6 the analytical conversion and the theoretical and real amount of hydroperoxide in the sample at the end of the experiment are shown.

Table 5.6: Conversion at different temperatures

temp. of experiment [°C]	analytical conversion [%]	theoretical amount of hydroperoxide [mole]	real amount of hydroperoxide [mole]	difference [mole]
5	98.5	0.58	0.34	0.24
10	100	0.55	0.31	0.24
20	76.1	0.98	0.53	0.45

The difference in the amount of hydroperoxide might of course be due to a non-representative sample but it is also well possible, that the difference is due to a decomposition of the hydroperoxide. For the product, the di-peroxide, it is very unlikely that its decomposition had started during the experiment, as the conversion is always close to 100%, except the experiment at 20°C, where it is possible that not only the hydroperoxide but also the di-peroxide started the decomposition. The increasing amount of mole hydroperoxide with temperature, which are „missing“ corresponds with an increasing reaction enthalpy with temperature.

The presented experiments in the RC1*e* all showed a tendency to a thermal runaway as there was always the possibility for the hydroperoxide to decompose. At the experiment at 20°C a runaway even occurred, but could be stopped. In order to achieve a safer process, further tests were performed with a diluted system. Therefore the reaction system was diluted with water as the first and most uncomplicated method. The diluted experiment was performed with 0.39mole solid; 1.22mole hydroperoxide and 2.1mole of catalyst, which was gradually added within 30min. To this system an amount of 150g water was added. In this case the heat production decreases immediately to zero with the end of the addition, on the other hand, no more di-peroxide is produced and the conversion was only 75.8%.

Then, another diluted experiment was performed with a very slight addition of water, 1.29mole solid; 3.22mole hydroperoxide and 3.86mole of catalyst. 50g water were added to dilute the system. The result can be seen in the following figure 5.21. It is first of all observable that the heat production decreases immediately with the end of the addition of the catalyst. The reaction can still not called addition-controlled, but the decrease in the heat release rate is faster than in the first, undiluted experiment at 10°C (see figure 5.18.). It decreases to almost zero within 50min after the addition. On the other hand the conversion was quite well, no larger amounts of intermediate were detected and the conversion was at 87% compared to 75.8% at the larger diluted process.

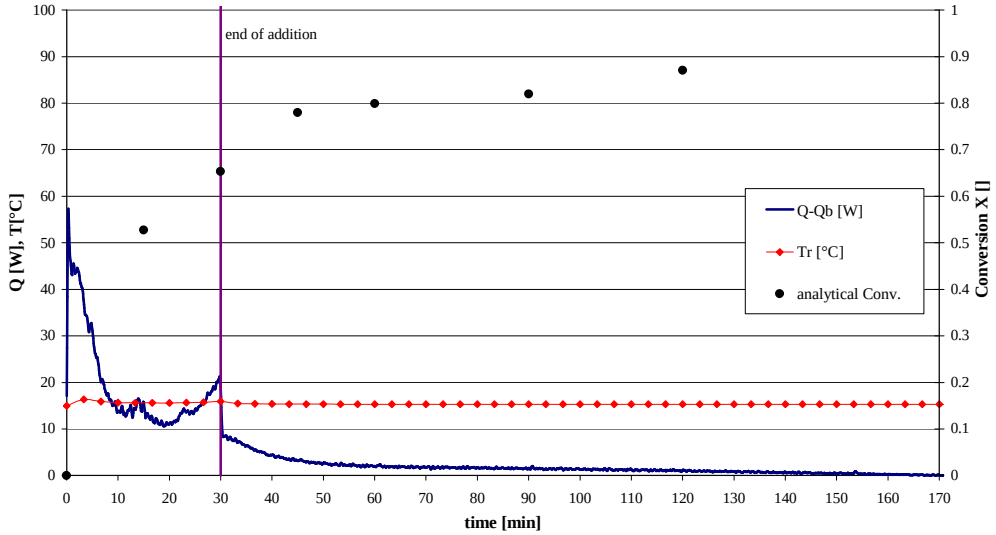


Figure 5.21: Diluted system in the RC1*e* at 15°C

The dilution with water in an open system gives also an inherent safety margin at 100°C as then the water will start to evaporate and cool off the system, always provided that there is a good condensing and reflux system. Besides the great advantage of a safer system the dilution had also disadvantages. The amount of product was reduced and the intermediate could be detected in the HPLC measurements in larger amounts and therefore shows that with the dilution an accumulation of unreacted substances occur. That an accumulation can be very critical for a semi-batch reaction due to the increase of the reaction rate with the then higher concentration, was already well described, for example by Steinbach [Steinbach 1] and Nomen [Nomen 1]. On the other hand a dilution can be helpful to lower the maximum temperature of the synthesis reaction [Nomen 2]. Apart from the reduced product the diluted process requires more effort in the separation and isolation of the product. It can be concluded that the process might not be performed economically in a great dilution.

For a short conclusion, the experiments in the RC1*e* showed that there is a parallel reaction to the synthesis, the decomposition of the hydroperoxide. Especially at higher temperatures of starting from 15°C a thermal runaway has therefore to be feared. Experiments with diluted systems showed that it might be helpful to add at least a small amount of water to the system to increase the safety of the synthesis reaction.

5.3. Analysis of the runaway reaction

The runaway reaction is usually analysed to get information about the „worst case“ scenario in a synthesis reaction. A „worst case“ scenario of the analysed synthesis reaction was tested in adiabatic batch reactors, first in a small laboratory adiabatic batch reactor with a dewar vessel of 0.5l content. After these tests the reaction was also performed at 1l-scale in the ADC II.

5.3.1. The runaway in the adiabatic batch reactor

First tests were performed on small scale. Approximately 0.05mole of solid and 0.13mole of hydroperoxide were given into the 0.5l dewar flask. Then the reaction was started by the immediate addition of approximately 0.15mole of catalyst. The resulting temperature curve was recorded which can be observed in the following diagram, figure 5.22. Various tests were performed and in almost all tests the phenomenon of a two step reaction mechanism was found. Obviously first the desired product was formed out of the solid and the hydroperoxide under release of heat. Then the temperature stayed stable for a period of time until the decomposition of the product and, as the reaction was operated in a slight excess of the hydroperoxide, possibly of the remaining hydroperoxide started. The period of time where the temperature stayed almost stable depended on the start temperature and of course on the amount of substance. In the presented experiment the maximum temperature of the synthesis was approximately 65°C, while the decomposition reached a temperature of 173°C. In about seven experiments, the decomposition always resulted in maximum temperatures between 150°C and 180°C.

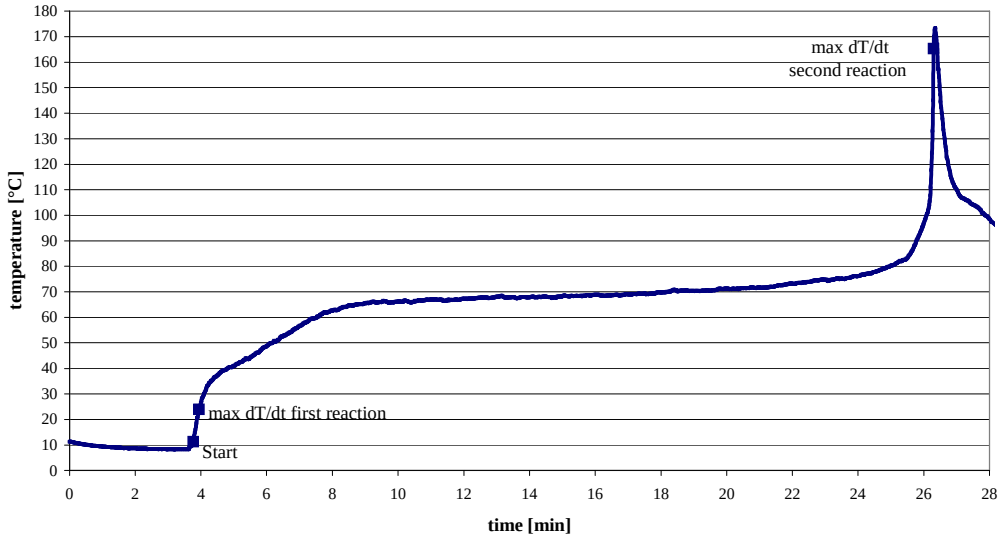


Figure 5.22: First test in an adiabatic batch reactor

The presented experiment had a start temperature of 9°C and the resulting maximum temperature for the first reaction was approximately 65°C and for the second reaction 173°C. The temperature difference between start temperature and maximum temperature was for the first reaction ΔT_1= 57K and for the second reaction (calculating from the maximum temperature of the first reaction) ΔT_2= 107K. Several experiments with equal amounts of substance at different start temperatures were performed. The resulting values can be observed in the following table 5.7.

Table 5.7: Different start temperatures in the adiabatic batch reactor

Start temperature [°C]	ΔT_{max} first reaction [K]	ΔT_{max} second reaction [K]
9	57	107
13.7	56	86
14	56	110
16	54	95
16	58	101

All measured temperatures are quite close together. The average ΔT of the synthesis reaction of the five experiments is 56.2°C, the average ΔT of the decomposition reaction is 99.8°C. From these tests again the conclusion can be drawn, that a decomposition of the peroxides has to be avoided under all circumstances.

With this information, a first estimation of the adiabatic temperature rise ΔT_{ad} for the synthesis reaction can be calculated. For an estimation of the reaction enthalpy and the adiabatic temperature rise of the synthesis reaction, first the Φ-factor of the system is needed. The Φ-factor is defined as the ratio of specific heat capacity of the whole system to the specific heat capacity of the sample:

$$\Phi = 1 + \frac{m_{dewar} \cdot c_{p,\,dewar}}{m_{sample} \cdot c_{p,\,sample}} \tag{5.12}$$

In the performed experiments a glass-dewar was used. The following specifications were used to calculate Φ:

$m_{dewar} \cdot c_{p,\,dewar} = 200J/K$ [Beyer 1], [Formell]

The value $m_{sample} \cdot c_{p,sample}$ can be calculated as follows:

$$(m_{sample} \cdot c_{p,\,sample}) = \Sigma(m_{component} \cdot c_{p,\,component}) \tag{5.13}$$

The heat capacity of the solid (0.8J/(g·K)) and the hydroperoxide (2J/(g·K)) were measured in the DSC, while the value of the catalyst was calculated according to the Nist webbook [NIST] to 1.98J/(g·K).
A value of
$10.65g_{(solid)} \cdot 0.8J/(g \cdot K) + 14.3g_{(hydroperoxide)} \cdot 2J/(g \cdot K) + 21.7g_{(catalyst)} \cdot 1.98J/(g \cdot K)$
= 80.2J/K resulted. In consequence the Φ-factor can be calculated:

$$\Phi = 1 + \frac{200\frac{J}{K}}{80.2\frac{J}{K}} = 1 + 2.49 = 3.49 \tag{5.14}$$

Having estimated the Φ-factor, the adiabatic temperature rise ΔT_{ad} can be calculated. As the maximum temperature rise is approximately 65°C for the first reaction, the adiabatic temperature rise would approximately be: $\Delta T_{ad} = \Phi \cdot \Delta T_{max} = 3.49 \cdot 65K = 227K$. This is obviously a much too high value. This high value is due to the relatively small amounts of substances which cause a high Φ-factor, which enlarges already small deviations. After

these first information on the maximum temperature and maximum rise in temperature of the synthesis reaction, an experiment was performed in the ADC II to get a precise information on the temperature and also information on the rise in pressure in a closed system.

5.3.2. Experiments in the ADC II

The experiments were performed with 60g solid and 108g hydroperoxide. Approximately 150g of catalyst was added with a pump within a minute at the beginning. The reaction started immediately with the addition. The dewar flask for the ADC II needs a minimum quantity of approximately 150ml volume, otherwise the stirrer and thermocouple do not plunge in the liquid. In the first experiment, the minimum amount of substance was calculated without any dilution and the experiment was started, relying on the emergency relief system. All substances and the dewar flask were cooled before the experiment, start temperature was about 3°C, stirring speed 750rpm. When the addition of the catalyst was started, the temperature and pressure rose steeply within seconds. The valve was supposed to open at a pressure of 15bar. It is not known, which pressure was achieved, the last value measured was about 13bar, when the dewar flask opened involuntarily. In the following figure 5.23 the curve of this test can be observed.

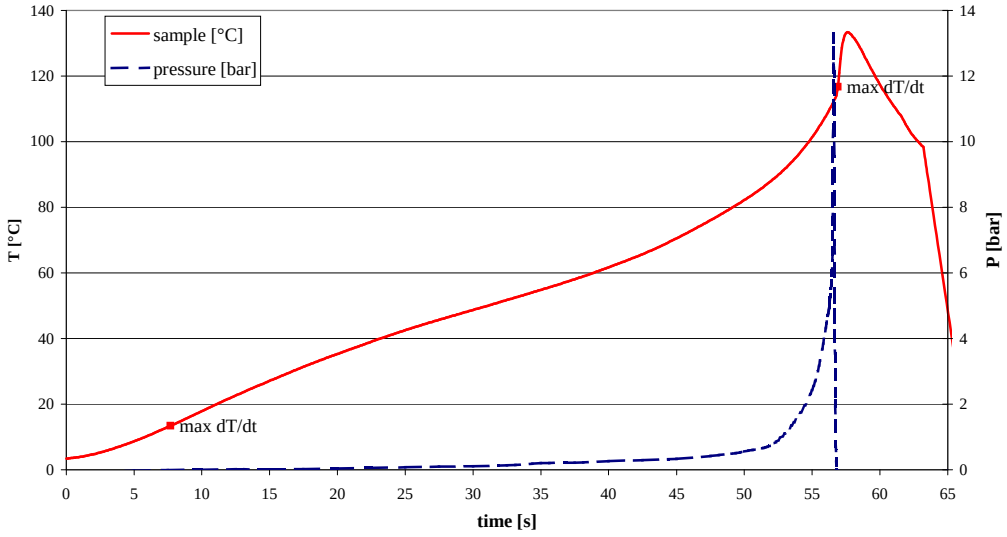


Figure 5.23: First experiment in the ADC II

From figure 5.23 it can be seen that the very fast reaction was followed by the decomposition of the product immediately.

The maximum temperature of the decomposition could not be measured, as the maximum pressure was higher than 15bar and the lid opened involuntarily. The last pressure measured was about 13bar, the highest temperature measured 133.3°C. It was also tried to distinguish the maximum rise in temperature for the first and the second reaction. The step from the first to the second reaction was fixed to be after 280s. The maximum rise in temperature for the first reaction is 12.7s after the start of the reaction. The maximum rise in temperature for the second reaction is 64.2s after the start of the reaction. The start is not visible in this diagram, as the computer program switched to another measuring mode with more values per minute after the first seconds.

For the first reaction of this experiment the adiabatic temperature rise ΔT_{ad} was again calculated. As already explained in chapter 5.3.1., the Φ-factor had to be calculated first. With the corresponding masses and heat capacities (see chapter 5.3.1.) of the substances and an estimation of $m_{dewar} \cdot c_{p,dewar} = 220J/K$ [Beyer 2], [Carter] the Φ-factor is:

$$\Phi = 1 + \frac{220\frac{J}{K}}{564\frac{J}{K}} = 1.4 \qquad (5.15)$$

With the help of the Φ-factor and the maximum difference in temperature for the first reaction ΔT_{max} the adiabatic temperature rise for the first reaction can be calculated as follows:

$\Delta T_{ad,\ synthesis} = \Phi \cdot \Delta T_{max} = 1.4 \cdot 43K = 60\ K$

This value is a lot lower than the one calculated from the glass dewar experiment in chapter 5.3.1. and much more reliable as the Φ-factor is much smaller. Possible small errors are not enhanced by the multiplication with a high Φ-factor.

The adiabatic temperature rise for the second reaction could not be calculated in the same way as the pressure rise was always too high for the equipment and the relief system had always to open so that no ΔT_{max} for the second reaction was observed.

However it was tried to evaluate the experiment concerning the secondary reaction. At the point of the maximum rise in temperature the total adiabatic rise in temperature is approximately to 45% completed [Steinbach 5]. Therefore the adiabatic temperature rise for the

second reaction could be estimated to 147K. With the help of this information, the end temperature can be approximated. According to the following equation: $X = (T - T_0)/\Delta T_{ad}$ even the conversion at a certain temperature can be calculated. This was done for the secondary reaction, which started at the inflection point at a temperature of 50.54°C after 31.5s of the experiment. With these further gained information it was tried to evaluate the experiment further and to determine therefore first an activation energy and a reaction rate constant.

The mass balance for the batch reactor can be written as follows [Baerns], [Hugo 2]:

$$\frac{dX_A}{dt} = (-\nu_a) \cdot \frac{r_{0,\infty}}{c_{a0}} \cdot \exp\left(\frac{-E_A}{RT}\right) \cdot \Phi(X) \tag{5.16}$$

Assuming a first order kinetics, the equation is:

$$k(T(t)) = \frac{dX}{dt} \cdot \frac{1}{(-\nu_a) \cdot (1 - X(t))} \tag{5.17}$$

Now the values for k(T(t)) can be calculated and the activation energy can be determined with the help of a diagram ln k versus 1/T. As:

$$\ln k(T) = \ln(k_\infty) - \frac{E_A}{R} \cdot \frac{1}{T} \tag{5.18}$$

the activation temperature is the gradient of the resulting straight line.

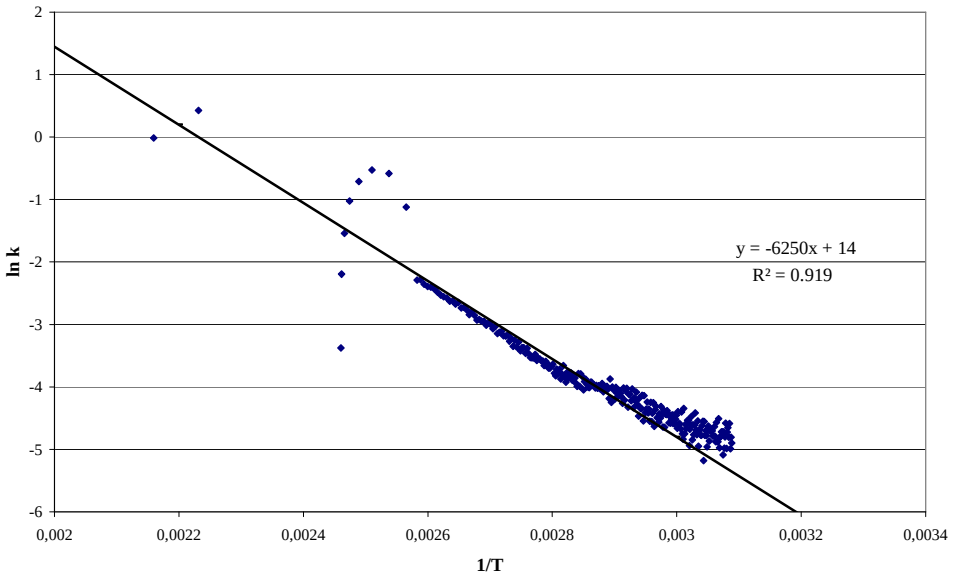


Figure 5.24: Determination of the activation temperature

The activation temperature was determined to 6250K and the reaction constant k_∞ determined to $1.2 \cdot 10^6$ 1/s. It has to be kept in mind here, that this decomposition is not only due to the hydroperoxide. The synthesis reaction was performed before and therefore existed already the di-peroxide, which was also decomposed completely, as no peroxide was found in the end of the experiment. Therefore the activation temperature is a mixture of the decomposition kinetics of the hydroperoxide and the di-peroxide.

As now the parameters for the reaction kinetics are known, the curve can be prolonged and the conversion can be calculated for every temperature. In the following figures 5.25 and 5.26 this prolongation and the resulting curve for the conversion can be observed. The start of the secondary reaction is at the inflection point at 31.5s and 50.54°C.

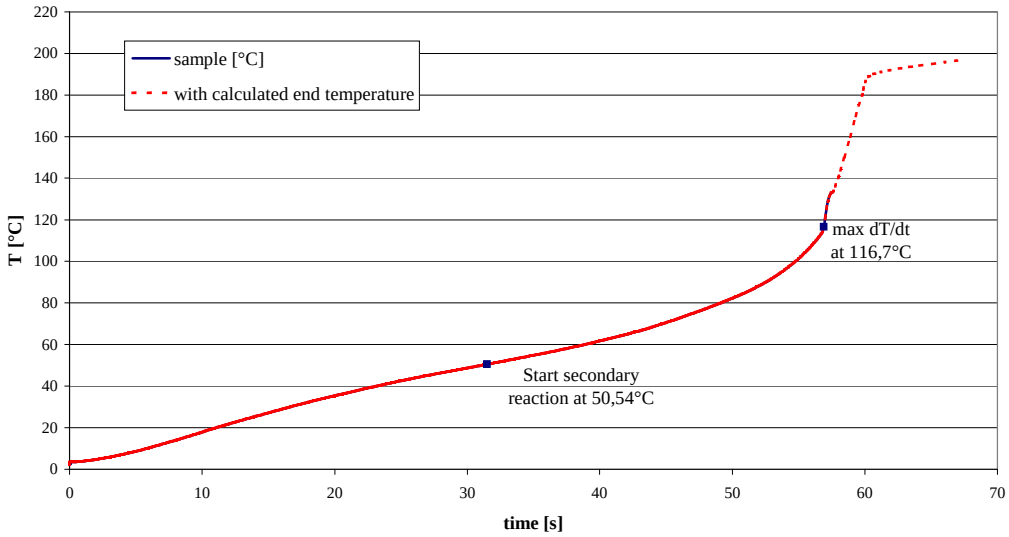


Figure 5.25: Prolongation of the temperature curve

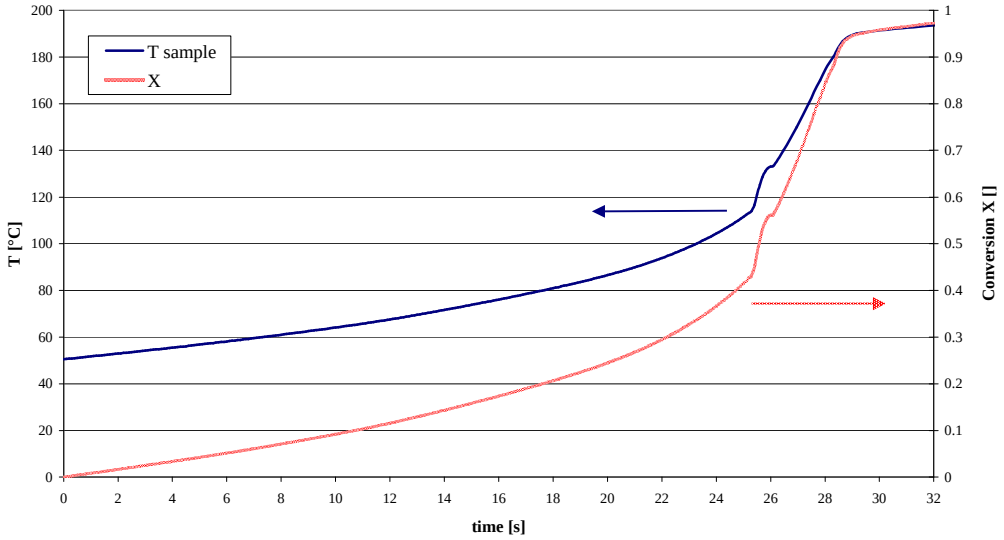


Figure 5.26: Resulting calculated conversion of the adiabatic experiment

To prove the results it had to be possible to re-simulate the original data. This was tried with the help of a software called Berkeley Madonna^{TM} [Marcey]. An adiabatic batch reactor was simulated with its corresponding mass and heat balance. For the heat balance the Φ-factor has of course to be considered, as the real reactor is not completely adiabatic. The heat balance is then:

$$\Phi \cdot \frac{dT}{dt} = \frac{\dot{Q}_{chem}}{V_R \cdot \rho \cdot c_p} \tag{5.19}$$

With dQ/dt_{chem} for a first order kinetics it can be written as:

$$\frac{dT}{dt} = \frac{k \cdot c_A \cdot \Delta_R H}{\Phi \cdot \rho \cdot c_p} \tag{5.20}$$

Now transforming the equation into a form, where it depends from the conversion and not the concentration any more with $c_A = c_{A0} \cdot (1\text{-}X)$ for a first order kinetics, one gets:

$$\frac{dT}{dt} = \frac{k \cdot c_{A0} \cdot (1 - X) \cdot \Delta_R H}{\Phi \cdot \rho \cdot c_p} \tag{5.21}$$

The mass balance for an adiabatic batch reactor for a first order kinetics, as well in a form, where it only depends on the conversion, can be written as:

$$\frac{dX}{dt} = k \cdot (1 - X) \tag{5.22}$$

With an already calculated Φ-factor of 1.4, an estimation of the value of $\rho \cdot c_p$ to 1700J/(K·l) and a calculated reaction enthalpy of this mixture (with approximately 0.309mole of di-peroxide formed and approximately resting 0.263mole hydroperoxide, which decompose) of -220kJ/mole the measured curves can well be simulated.

The result of this attempt can be seen in the following figure 5.27. The figure verifies the calculated reaction kinetics of first order for the mixture of hydroperoxide and di-peroxide, as the simulated data follow quite well the original data.

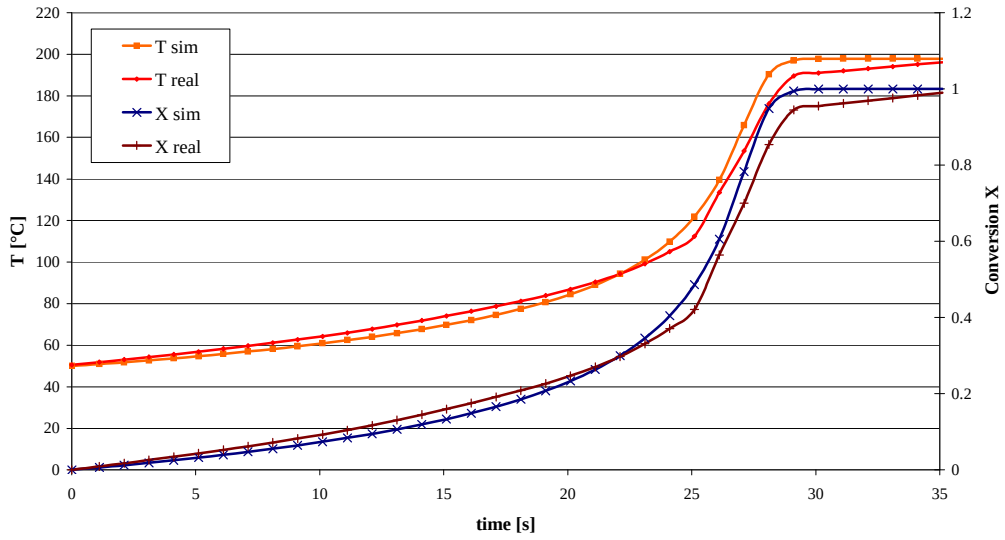


Figure 5.27: Original and re-simulated data

As the system reacted this violent, it was diluted with water to slow down the reaction rate and it was operated in an open system to prevent a rupture of the sample container. As it is then open, the system is not completely adiabatic any more. The reaction mixture was 56.09g hydroperoxide, 25g solid, 55.3g water and 89.27g catalyst. The resulting curve can be observed in the following figure 5.28.

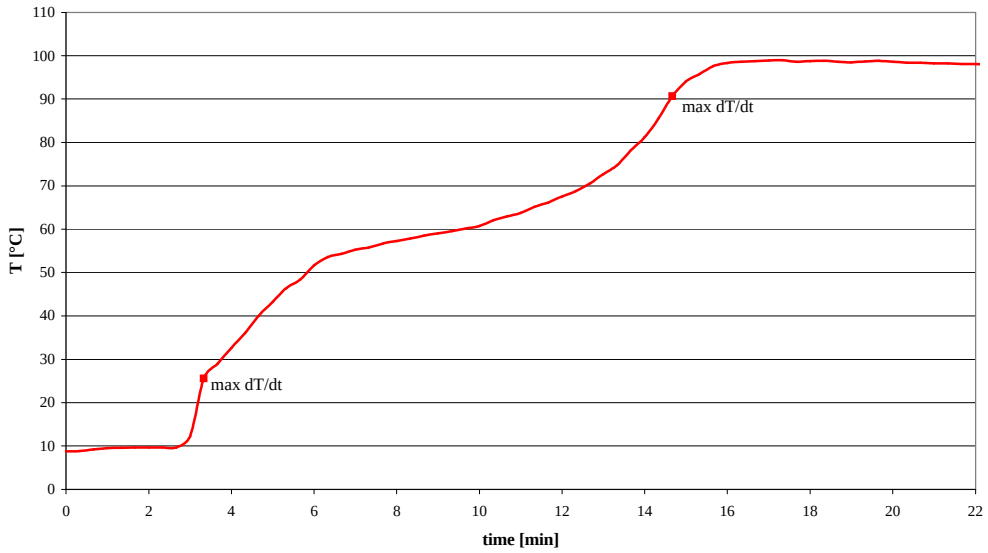


Figure 5.28: „Adiabatic test“, diluted with water, in an open system

In the diagram of the diluted system two reactions can be observed as well. After the desired reaction was completed, a decomposition took place. As the system was diluted with water, the rise in temperature stopped at 100°C due to the evaporation of the water. Therefore it can be said that with the dilution with water an inherent safety margin is created, as the evaporation of the water cools off the system. But this implies of course an open system and a very well constructed condensing and reflux system, otherwise the reaction rate will increase rapidly after all water evaporated and a thermal runaway can again be feared.

Chapter 6:

Simulations

6.1 Introduction

After the experimental analysis of a process its corresponding parameters have to be evaluated. With the knowledge of all characteristics of the process, resimulations of the experiments have to be made, to verify the determined results. If the resimulations are successful, the characterising process parameters are assumed to be correct. In this case further simulations can be performed to predict the behaviour of the reaction at different process conditions. This is important for a scale-up of the process, as it is more economic and safer to test the next scale first in a simulation.

To make a sensible simulation, first the kinetics and the kinetic parameters of the reaction have to be known. In the present work the aim was to resimulate the results of the experiments in the RC1*e* as this calorimeter resembles the reactors in industrial scale. It was of course started with the determination of reaction kinetics.

6.2 Determination of reaction kinetics

As already described in chapter 5.2. the reaction system cannot be described by simple formal kinetics as there is a second reaction parallel to the desired synthesis reaction. This parallel reaction is the decomposition of the hydroperoxide which is also catalysed by the added catalyst. It was therefore assumed that this second reaction does not have a great relevance in the beginning of the synthesis but later with lesser solid as a reaction partner becomes more important.

Furthermore the synthesis reaction itself consists of two steps, first the reaction of the solid with a hydroperoxide to the intermediate and second the reaction of the intermediate with the hydroperoxide to the di-peroxide. To keep the model as simple as possible, it will be tried first to describe the synthesis reaction in a summarized way and therefore only with one reaction kinetics.

The produced di-peroxide might as well decompose, but as its maximum temperature according to the 100K-rule of 32°C (see chapter 5.1) is higher than the process temperature and the conversion was usually close to one, its decomposition is neglected in the model. As the solid does not show a decomposition, no further parallel reaction will be regarded.

It was therefore worked with a simultaneous reaction system where the first reaction is the decomposition of the hydroperoxide and the second reaction is the desired synthesis of the di-peroxide. The reaction mechanisms are assumed to be in the following way:

I. 1 hydroperoxide + catalyst $\rightarrow$ 1 decomposition product + catalyst

II. 1 solid + 2 hydroperoxide + catalyst $\rightarrow$ 1 di-peroxide + 2 water + catalyst

The reaction enthalpy for the first reaction is known. The reaction enthalpy was measured in the DSC (see chapter 5.1.1.) with $\Delta_R h$= -172.8kJ/mole. The reaction kinetics for the first reaction was calculated from the results in the adiabatic batch reactor ADC II. A formal reaction kinetics of first order was found with an activation temperature of E/R = 6250K and a reaction constant of $k_\infty = 1.2 \cdot 10^6$l/s. These determined reaction kinetics might also consider the decomposition of the di-peroxide, as in the ADC II experiment first the synthesis took place before the decomposition started. This means that the determined reaction kinetics for the hydroperoxide are not totally reliable. On the other hand, in this reaction kinetics the catalytic effect of the catalyst is considered, which is important, as the decomposition mainly takes place when all catalyst is added. Therefore it is assumed that these reaction kinetics for the first reaction are a good first estimation.
The reaction enthalpy for the second reaction can be determined with the help of the experiments in the RC1*e*. The reaction kinetics for the second reaction were unknown and had to be determined.

To describe the two parallel reactions together, two parameters called reaction progress variables, ξ, are needed. These parameters ξ give the progress of each of the two parallel reactions and resembles the conversion x for a singular reaction. For the determination of the progresses of reaction ξ_1, ξ_2 for the two reactions, a key component, which only exists in one reaction, for each reaction has to be chosen and the mass balance for each substance has to be put up.

For the concerning reactions:

I. 1 hydroperoxide(=C) + catalyst $\rightarrow$ 1 decomposition product(=D) + catalyst

II. 1 solid(=B) + 2 hydroperoxide(=C) + catalyst $\rightarrow$ 1 di-peroxide(=E) + 2 water + catalyst

the decomposition product (=D) is chosen as the key component of reaction I and the di-peroxide (=E) is chosen as key component of reaction II.

The stoichiometric coefficients ν_{kr} with k for the component and r for the reaction are then as follows:

$k_1 = D$; $k_2 = E$; $k_3 = C$; $k_4 = B$;

$\nu_{11} = 1$; $\nu_{21} = 0$; $\nu_{31} = -1$; $\nu_{41} = 0$;

$\nu_{12} = 0$; $\nu_{22} = 1$; $\nu_{32} = -2$; $\nu_{42} = -1$;

With $n_k = n_{k0} + n_0 \cdot \sum \nu_{kr} \cdot \xi_r$ and $n_0 = n_{C0} + n_{B0}$,

the mass balances give:

$n_C = n_{C0} + n_0(-2\xi_2 - \xi_1)$;

$n_B = n_{B0} + n_0(-\xi_2)$;

$n_D = n_0 \cdot \xi_1$;

$n_E = n_0 \cdot \xi_2$.

It is further known that the first reaction is of first order kinetics:

$r_1 = k_1 \cdot c_C \cdot c_{cat}$; with c_{cat} only depending on the addition, constant with end of addition.

The order of the second reaction is more complex, the reaction rate r is assumed to depend on the concentration of the solid, hydroperoxide and catalyst as follows:

$r_2 = k_2 \cdot c_C^2 \cdot c_B \cdot c_{cat}$.

The parameter ξ_2 could be calculated out of the measurements of the di-peroxide measured with the help of the HPLC. The determination of ξ_1 was a bit more difficult, as the decomposition product was not measured in the HPLC. Therefore ξ_1 is approximated from the mass balance. To determine ξ_1 the amount of the decomposition product has to be calculated: $n_D = n_{C0} - 2n_E$ ($=n_{C \text{ bound in the di-peroxide}}$)- $n_{C \text{ bound in the intermediate}}$ $-n_C$
the initial value of hydroperoxide minus the hydroperoxide bounded in the di-peroxide and in the intermediate (which could only be estimated) gives the theoretical amount of hydroperoxide in the solution. The difference between the theoretical amount and the measured (usually lower) amount of hydroperoxide gave the amount of hydroperoxide which was already decomposed.

The values of ξ_1 and ξ_2 could then be calculated for each reaction. In the following diagram 5.26 the ξ_1 is shown over ξ_2 for the experiments at 5, 10 and 15°C.

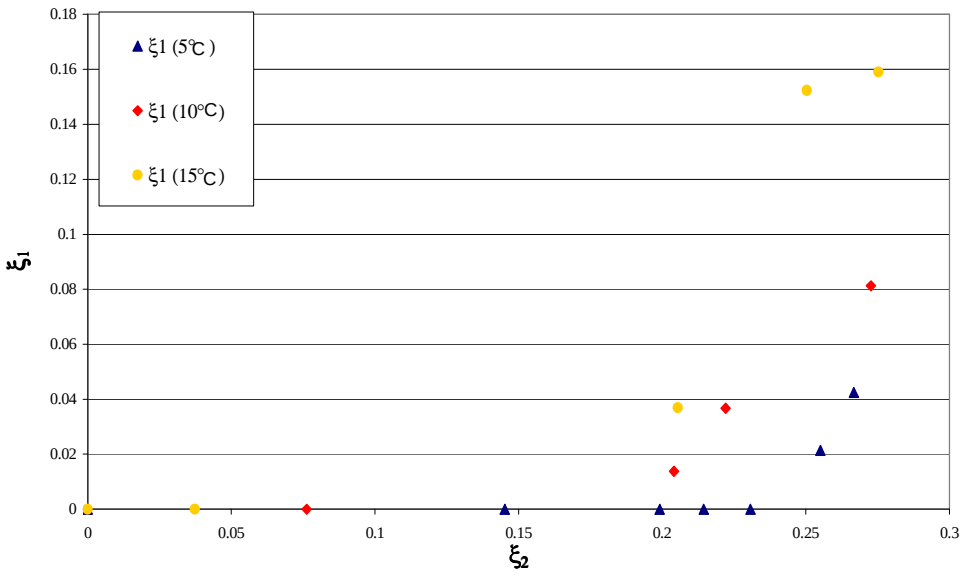


Figure 6.1: ξ_1 over ξ_2 at 5, 10 and 15°C

From this figure it is clearly visible that the decomposition reaction dominates in the end of the experiments. Obviously first the synthesis reaction was favoured until all solid was at least transformed into the intermediate product. Then the catalyst enhanced the decomposi-

tion. The figure also shows that the decomposition increased with increasing temperature. But in all experiments in the first part only the synthesis reaction took place. This first part was longer in the experiments at lower temperatures.

The reaction enthalpy could be calculated according to the following rule [Baerns, 1987]:

$\Delta_R H_\Sigma[J] = \Delta_R h_1[J/mole]\cdot\xi_1\cdot n_0[mole] + \Delta_R h_2[J/mole]\cdot\xi_2\cdot n_0[mole]$

In the following table 5.7 the parameters and the calculated values for the reaction enthalpy for the synthesis reaction are shown. The experiment at 15°C differed a little from the other experiments, as it was slightly diluted. That is the reason why the ξ_1 in this experiment is the lowest of all experiments, as with the dilution the decomposition is lowered.

Table 6.1: Determination of the reaction enthalpy of the synthesis

T [°C] of experiment	**ξ_1 at the end**	**ξ_2 at the end**	**$\Delta_R H_\Sigma$ [J]**	**n_0 [mole]**	**$\Delta_R h_2$ [J/mole]**
5	0.0425	0.2667	$5.64\cdot10^4$	3.86	$2.72\cdot10^4$
10	0.0813	0.2727	$9.16\cdot10^4$	3.86	$3.55\cdot10^4$
15 (dil.)	0.0126	0.2489	$5.25\cdot10^4$	4.51	$3.81\cdot10^4$

It resulted an average reaction enthalpy for the second reaction of $\Delta_R h_2$=-33.6kJ/$mole_{solid}$ as the solid is the limiting component for the synthesis reaction. With the help of the determined reaction enthalpy it was then tried to determine the pre-exponential factor k_∞ and activation temperature E/R.

Two different methods were used to determine the reaction kinetics of the synthesis reaction, which will be both presented in the following, starting with the first.

For the first method, a closer look was taken at the figure 5.26. It can be observed there, that in the first part of all experiments only the synthesis reaction took place. If it is assumed that in the beginning only the synthesis reaction takes place, the heat production of the synthesis reaction can be described as follows:

$$\dot{Q} = -\Delta_R H \cdot r \cdot V \qquad (6.1)$$

With the reaction rate of the synthesis reaction $r_2=k_2 \cdot c_{solid} \cdot c^2_{hydroperoxide} \cdot c_{catalyst}$, the reaction rate constant k_2 can be described with the following equation:

$$k_2 = \frac{\dot{Q}}{-\Delta_R H \cdot V \cdot c_{solid} \cdot c^2_{hydroperoxid} \cdot c_{catalyst}} \tag{6.2}$$

Now the k_2 could be calculated for each experiment in the part where only the synthesis reaction took place. Out of the calculated values for k_2 at different temperatures the pre-exponential factor and activation temperature can be determined following Arrhenius, as:

$$\ln k = \ln k_\infty - \frac{E}{RT} \tag{6.3}$$

In the following diagram, figure 5.27, the resulting determination of the pre-exponential factor k_∞ and activation temperature E/R is shown.

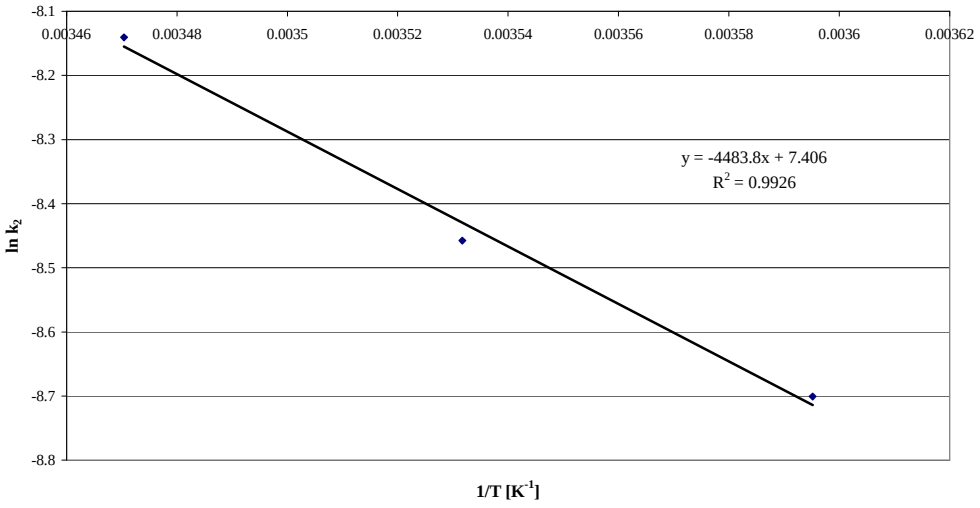


Figure 6.2: Determination of the kinetic parameters of the second reaction

As can be observed in the diagram, an activation temperature of E/R=4484K resulted. The pre-exponential factor was calculated to $1.6 \cdot 10^3 l^3/(mole^3 \cdot s)$.

Now the second method to determine the reaction kinetic and their parameters for the synthesis reaction was tried. The second method tried to determine the kinetic parameters E/R and k_∞ for the second reaction with the help of the determined ξ_1 and ξ_2.

It is known [Hugo 1] that:

$$\frac{d\xi_2}{d\xi_1} = \frac{r_2}{r_1} \tag{6.4}$$

$d\xi_1$ and $d\xi_2$ can be calculated from the following equation:

$$\frac{dc_k}{dt} = (-\nu_{kr}) \cdot r_r \tag{6.5}$$

with index r for the concerned reaction and k for the component.
For ξ_1 it can therefore be calculated:

$$\frac{dc_D}{dt} = k_1 \cdot c_C \cdot c_{cat} \tag{6.6}$$

$$\frac{dn_D}{Vdt} = \frac{k_1 \cdot n_C \cdot n_{cat}}{V^2} \tag{6.7}$$

$$\frac{n_0 d\xi_1}{dt} = \frac{k_1 \cdot n_C \cdot n_{cat}}{V} \tag{6.8}$$

$$\frac{d\xi_1}{dt} = \frac{k_1 \cdot n_C \cdot n_{cat}}{V \cdot n_0} \tag{6.9}$$

ξ_2 can be calculated in the same way to:

$$\frac{d\xi_2}{dt} = \frac{k_2 \cdot n_B \cdot n_{cat} \cdot n_C^2}{n_0 \cdot V^3} \tag{6.10}$$

As there was no other way to determine the reaction kinetics of the decomposition of the hydroperoxide, those data determined with the help of the simulation in the following chapter 6.3. were used. The activation temperature for the decomposition is therefore $1.37 \cdot 10^4$K and the pre-exponential factor $2.87 \cdot 10^{14}$l/(mole·s). As now all data are known except the k_2, it should be possible to calculate k_2 for each experiment. Unfortunately there were too less analytical data available to calculate sensible data. Further it was noted that the shape of the curves ξ_1 over ξ_2 is unusual. As can be verified from Steinbach [Steinbach 2], those curves never have an s-shape but an exponential gradient. Those curves were therefore first fitted with an exponential function, as can be observed in the following three figures 6.3, 6.4, 6.5.

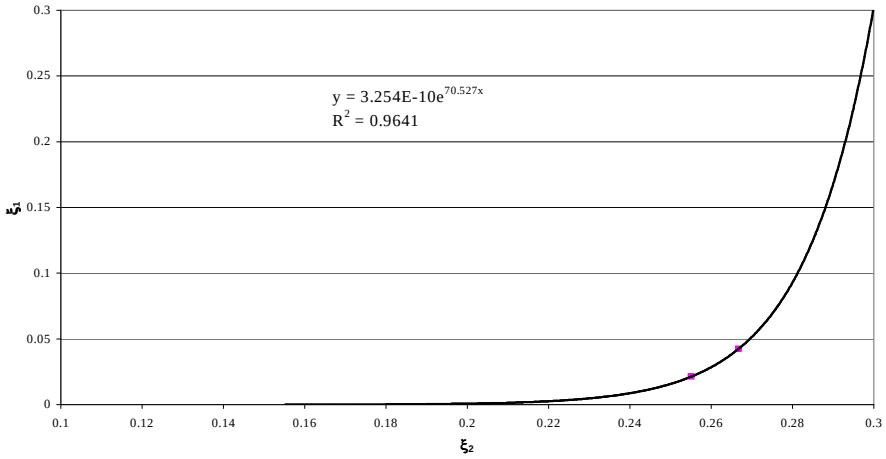


Figure 6.3: ξ_1 over ξ_2 at a temperature of 5°C

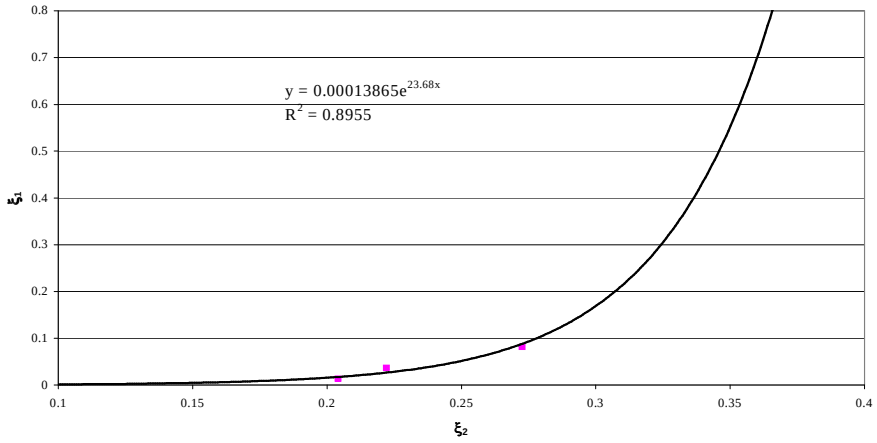


Figure 6.4: ξ_1 over ξ_2 at a temperature of 10°C

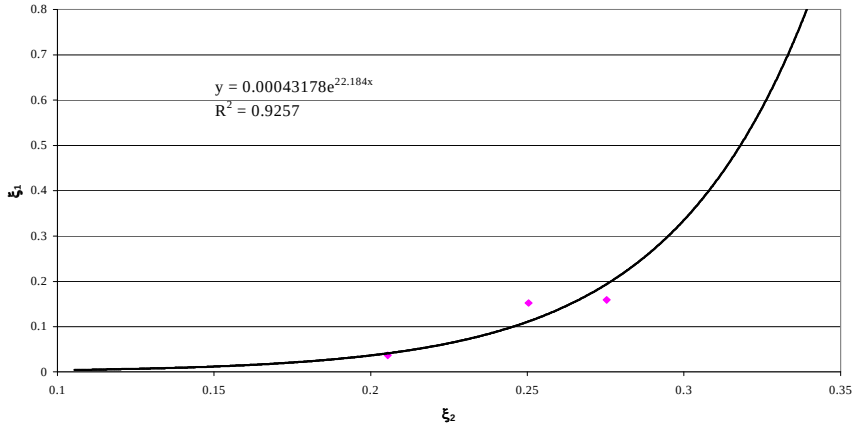


Figure 6.5: ξ_1 over ξ_2 at a temperature of 15°C

With the resulting curves the corresponding values for ξ_1, ξ_2 as well as $d\xi_1/dt$ and $d\xi_2/dt$ can be calculated for each temperature. According to equation (6.4) and the equations (6.9) and (6.10) the unknown parameter k_2 can be calculated as follows:

$$k_2 = \frac{d\xi_2}{d\xi_1} \cdot \frac{k_1 \cdot V^2}{n_C \cdot n_B} \tag{6.11}$$

where V is the actual volume of the semi-batch reactor and k_1 the reaction rate constant of the decomposition. The corresponding values for k_2 are calculated for each temperature (at 5, 10 and 15°C). Unfortunately the values for k_2 for the experiment at 5°C differed too much and were therefore not used. With the help of the Arrhenius-diagram, which can be observed in the following figure 5.31, the kinetic parameters activation temperature E/R and pre-exponential factor k_∞ can then be calculated out of the two experiments at 10°C and 15°C.

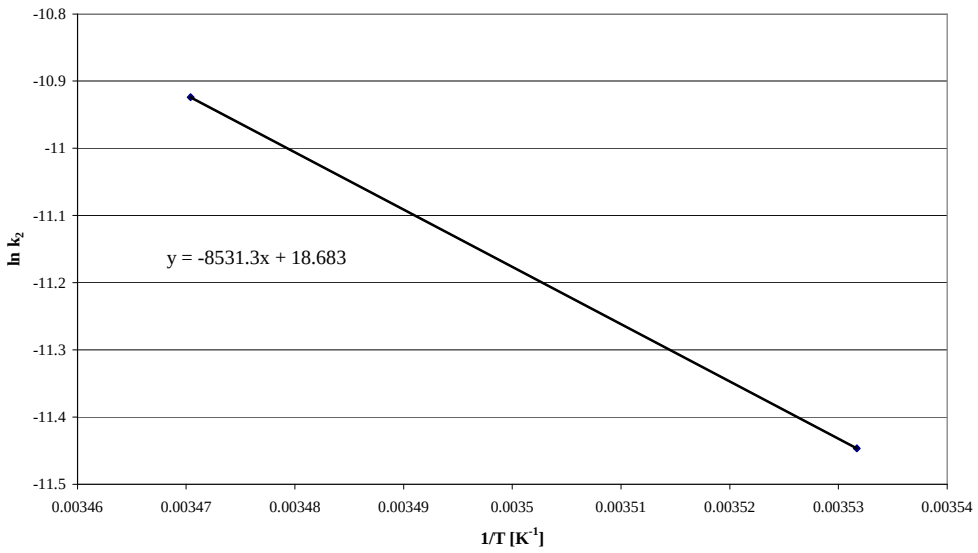


Figure 6.6: Determination of E/R and k_∞ for the synthesis reaction

With this diagram E/R could be determined to 8531K and k_∞ to $1.3 \cdot 10^8 l^3/(mole^3 \cdot s)$. As these values were determined with only two points, they might not be totally reliable and have to be treated carefully. This seems in the first moment to be too different from the reaction kinetics determined with the first method, but as will be shown later in chapter 6.3. both determined kinetic parameters have their right to exist. For a better overview, the

determined kinetic parameters with the two different methods are again presented in the next table 6.3.

Table 6.2: Determined kinetic parameters for the (single) synthesis reaction

Method	Comments	E/R [K]	k_∞ [$l^3/(mole^3 \cdot s)$]
1	Determination in the beginning of the process, parallel decomposition of the hydroperoxide is neglected	4484	$1.6 \cdot 10^3$
2	Determination with the help of ξ_1 and ξ_2 after a few minutes after the start of the reaction	8531	$1.3 \cdot 10^8$

6.3. Simulation of the RC1*e* experiments

For the simulation of the RC1*e* experiments the software Berkeley Madonna [Marcey] was used. It was tried to simulate the performed experiments in the RC1*e* with a model of a simultaneous reaction.

According to Hugo [Hugo 1], the mass balance for a simultaneous reaction can be described as follows:

$$\frac{dn_k}{dt} = V \cdot \sum_r (\nu_{kr} \cdot r_r) \tag{6.12}$$

The mass balance for the solid is therefore:

$$\frac{dn_B}{dt} = -\frac{k_2 \cdot n_B \cdot n_{cat} \cdot n_C^2}{V^3} \tag{6.13}$$

and the mass balance for the hydroperoxide can be written as:

$$\frac{dn_C}{dt} = -k_1 \cdot \frac{n_C \cdot n_{cat}}{V} - 2 \cdot \frac{k_2 \cdot n_C^2 \cdot n_{cat} \cdot n_B}{V^3} \tag{6.14}$$

with the volume as the actual volume of the semi-batch reactor.

The heat release of the chemical reactions can be written as follows:

$$\dot{Q}_{total,\,chem} = (-\Delta_R H_1) \cdot k_1 \cdot \frac{n_C \cdot n_{cat}}{V} + (-\Delta_R H_2) \cdot k_2 \cdot \frac{n_C^2 \cdot n_B \cdot n_{cat}}{V^3} \tag{6.15}$$

The heat balance is equivalent to (see chapter 4.2.2 for the description of the formula):

$$\dot{Q}_{total,\,chem} = \dot{Q}_{akku} - \dot{Q}_j - \dot{Q}_{add} - \dot{Q}_{loss} \tag{6.16}$$

The heat balance for the concerned experiments can be written as follows:

$$\dot{Q}_{total,\,chem} = -\dot{Q}_j \tag{6.17}$$

The heat release rate of the addition dQ/dt_{add} was not considered here. The temperature of the added catalyst was kept equal to the isothermal reaction temperature and therefore no heat is introduced. The dissolution heat produced by the added catalyst was already considered in the reaction enthalpy of the synthesis reaction. Therefore dQ/dt_{add} can be neglected here.

Equation (6.17) can also be written as follows:

$$(-\Delta_R H_1) \cdot k_1 \cdot \frac{n_C \cdot n_{cat}}{V} + (-\Delta_R H_2) \cdot k_2 \cdot \frac{n_C^2 \cdot n_B \cdot n_{cat}}{V^3} = -(k_w \cdot A \cdot (T_j - T_R)) \tag{6.18}$$

With the presented heat and mass balances the simultaneous reaction was simulated with the help of the software Berkeley Madonna [Marcey].

The results of the first simulation of the experiment at 5°C can be observed in the following figure 6.7.

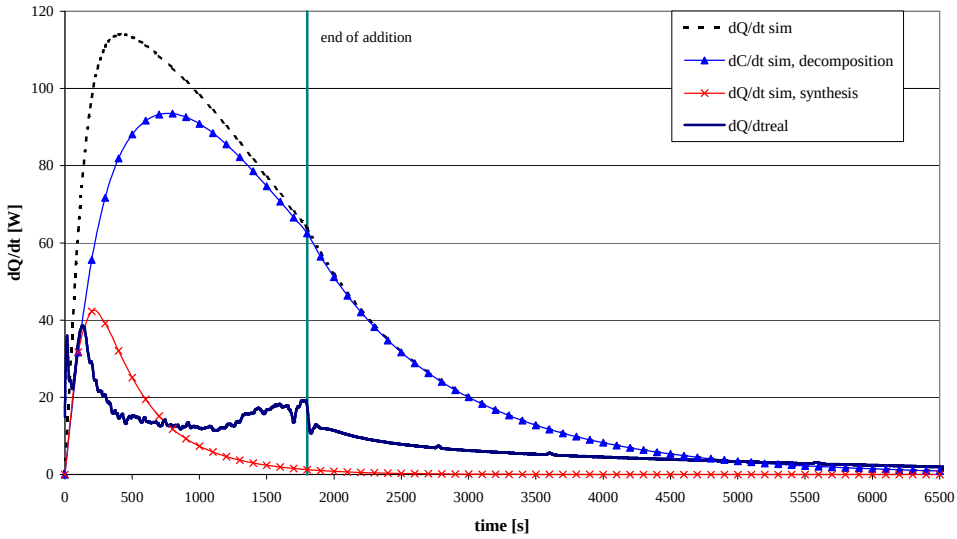


Figure 6.7: First simulation of the experiment at 5°C

In the following table 6.3 all used parameters are presented.

Table 6.3: Parameters used for the first simulation

Parameter	Value
E/R first reaction	6250K
E/R second reaction	4484K
k_∞ first reaction	$1.2 \cdot 10^6$l/s
k_∞ second reaction	$1.6 \cdot 10^3$l/mole·s
Δ_Rh first reaction	-172.8kJ/mole
Δ_Rh second reaction	-33.6kJ/mole
addition time	30min

The diagram in figure 6.7 shows that the simulation of the heat release does not show a good shape, which allows the assumption that the kinetic models have to be changed. The simulated heat release is much too high. The simulated value for the total amount of released heat gives about -231kJ, while the measured value is about -56kJ and therefore only approximately 24% of the simulated value. A closer look at all simulated data showed that in the simulation all hydroperoxide is consumed while some solid is left, a result completely different from the experiments. In the experiments it was observed that first all solid was used up until the decomposition and therefore a strong consumption of the hydroperoxide started. Further it was obvious that the high heat release rate was due to the complete decomposition of the hydroperoxide, which could not be found either in reality.

The figure 6.7 showed clearly that the assumption of this first model are not valid, too many simplifications were made. The model had therefore to be changed to fit the heat release function. A closer look was taken at the synthesis reaction. In all sample analysis in the HPLC the intermediate product was found, therefore it was concluded that the two-step reaction mechanism of the synthesis should not be neglected. The reaction system was then divided into three reactions as follows:

I. 1 hydroperoxide(=C) + catalyst → 1 decomposition product(=D) + catalyst

II. 1 solid(=B) + 1 hydroperoxide(=C) + catalyst → 1 intermediate(=IM) + 1 water + catalyst

III. 1 intermediate(=IM) + 1 hydroperoxide(=C) + catalyst → 1 di-peroxide(=E) + 1water + catalyst

It was observed that the decomposition of the hydroperoxide is strongly dependent on the concentration of the catalyst. This was considered with an exponent p on the concentration of the catalyst. This is then of course not a realistic model for the decomposition, but as can be observed later, represents very well the strong dependency on the catalyst.

This changes the heat and mass balance to the following, the heat balance now is:

$$(-\Delta_R H_1)\cdot k_1 \cdot \frac{n_C \cdot n_{cat}^p}{V^p} + (-\Delta_R H_2)\cdot k_2 \cdot \frac{n_C \cdot n_B \cdot n_{cat}}{V^2} + (-\Delta_R H_3)\cdot k_3 \cdot \frac{n_C \cdot n_{IM} \cdot n_{cat}}{V^2} = -k_w \cdot A \cdot (T_j - T_R) \tag{6.19}$$

the mass balance for the solid is now written as:

$$\frac{dn_B}{dt} = -\frac{k_2 \cdot n_B \cdot n_{cat} \cdot n_C}{V^3} \tag{6.20}$$

the mass balance for the hydroperoxide is now written as:

$$\frac{dn_C}{dt} = -k_1 \cdot \frac{n_C \cdot n_{cat}^p}{V^p} - k_2 \cdot \frac{n_C \cdot n_{cat} \cdot n_B}{V^2} - k_3 \cdot \frac{n_C \cdot n_{cat} \cdot n_{IM}}{V^2} \tag{6.21}$$

and the mass balance for the intermediate is written as:

$$\frac{dn_{IM}}{dt} = k_2 \cdot \frac{n_C \cdot n_{cat} \cdot n_B}{V^2} - k_3 \cdot \frac{n_C \cdot n_{cat} \cdot n_{IM}}{V^2} \tag{6.22}$$

Then the simulations with this new model are performed in Berkeley Madonna [Marcey], where the parameters k_1, k_2, k_3 and p are fitted to agree with the measured curves. In the following figure 6.8 this simulation with already fitted parameters of the experiment at 5°C is shown and in the following table 6.4 the finally used parameters are shown.

Table 6.4: Parameters for the simulation in figure 6.8

Parameter	Value
k1 (first reaction = decomposition of hydroperoxide)	$1.2 \cdot 10^{-7} l^{4.6}/mole^{4.6} \cdot s$
k2 (second reaction = formation of intermediate)	$1.4 \cdot 10^{-3} l^{2}/mole^{2} \cdot s$
k3 (third reaction = formation of di-peroxide)	$1.39 \cdot 10^{-4} l^{2}/mole^{2} \cdot s$
$\Delta_R h$ first reaction	-172.8kJ/mole
$\Delta_R h$ second reaction	-16kJ/mole
$\Delta_R h$ third reaction	-16kJ/mole
parameter p	4.6
addition time	30min

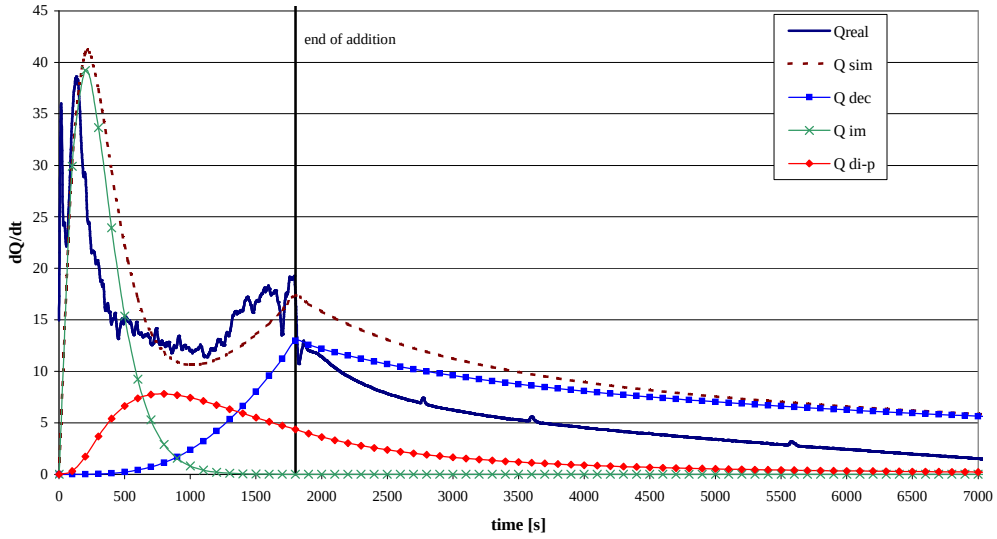


Figure 6.8: Simulation of the experiment at 5°C with the second model

The diagram shows a good agreement between simulated and measured data. The first step of the reaction is the production of the intermediate (Qim). This first step is very fast and could also be observed during the experiments, as within the first 10-15min the solid disappeared and only a liquid-liquid solution was found. With a short delay also the production of the di-peroxide starts (Qdi-p), most of the product is already produced with the end of the addition, after the addition the production is quite slow. With an even greater delay the decomposition of the di-peroxide starts, this is due to its higher activation temperature and

its strong dependency on the catalyst. The decomposition has its maximum at the end of the addition. The curves of the measured heat release rate (Qreal) and the simulated heat release rate (Qsim) show a good agreement except for the part after the end of the addition. In this part the heat release rate falls stronger in reality than in the simulated curves. This is supposed to be due to the fact that in reality the catalyst releases a dissolution heat when added to the reaction system, as already described in chapter 5.2., which of course stops immediately with the end of the addition and was not considered in the simulation model.

The best agreement for the curves was achieved with the following parameters: $k_1=1.2\cdot10^{-7}l^{4.6}/(mole^{4.6}\cdot s)$, $k_2=1.4\cdot10^{-3}l^2/(mole^2\cdot s)$, $k_3=1.39\cdot10^{-4}l^2/(mole^2\cdot s)$ and p=4.6. Also the total released heat was due to the too high decomposition of the hydroperoxide with (-85.6kJ) much higher than the measured released heat of (-56kJ), but much better than in the first attempt.

In the following figure 6.9 the mole of substances over time are shown and it can be observed, that there is as well a good agreement between the measured and the simulated data.

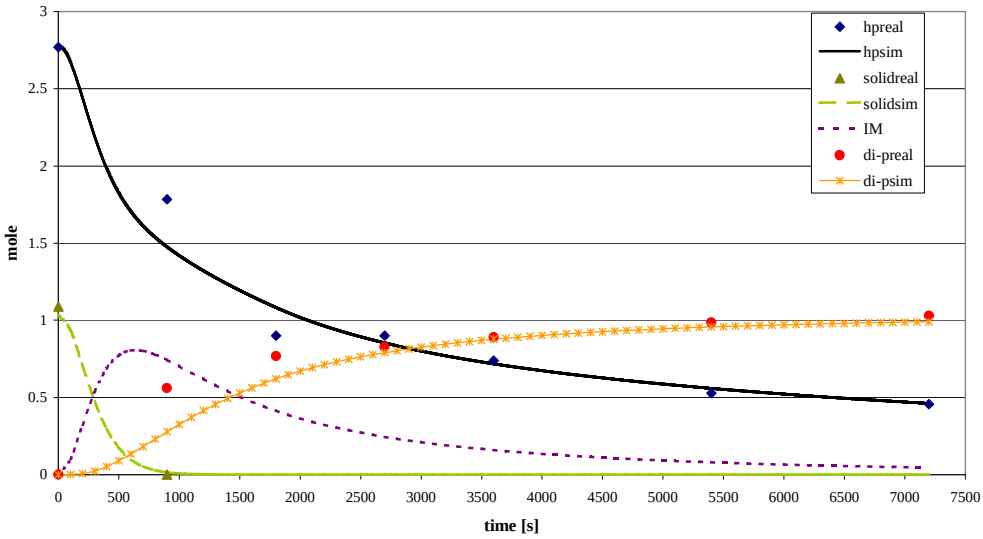


Figure 6.9: Simulation at 5°C, amount of educts and products

The experiments at 10°C and 15°C were fitted in the same way, only the parameter p=4.6 was kept constant. With the resulting values for the parameters k_1, k_2 and k_3 and the corresponding Arrhenius-plot the activation temperature and the pre-exponential factor were

calculated for each reaction. In the following three figures 6.10, 6.11 and 6.12 the Arrhenius plots are shown.

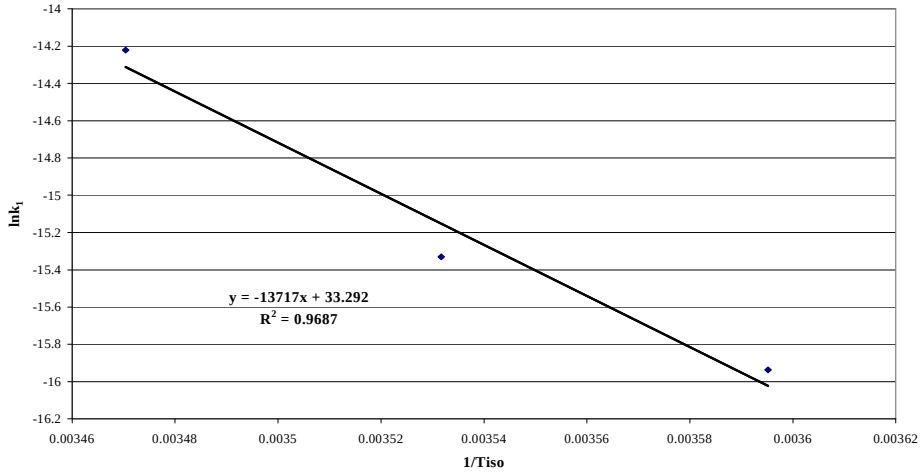


Figure 6.10: Arrhenius plot for k_1

The kinetic parameters for the first reaction, i.e. the decomposition was therefore determined to E/R= $1.37 \cdot 10^4$K and $k_\infty = 2.874 \cdot 10^{14} l^{4.6}/(mole^{4.6} \cdot s)$. The data for the activation temperature correspond quite well with the activation temperature of $1.26 \cdot 10^4$ K determined with the help of the isothermal measurements in the DSC (see also chapter 5.1.). The value for the pre-exponential factor cannot be compared, as there was no other method to calculate it.

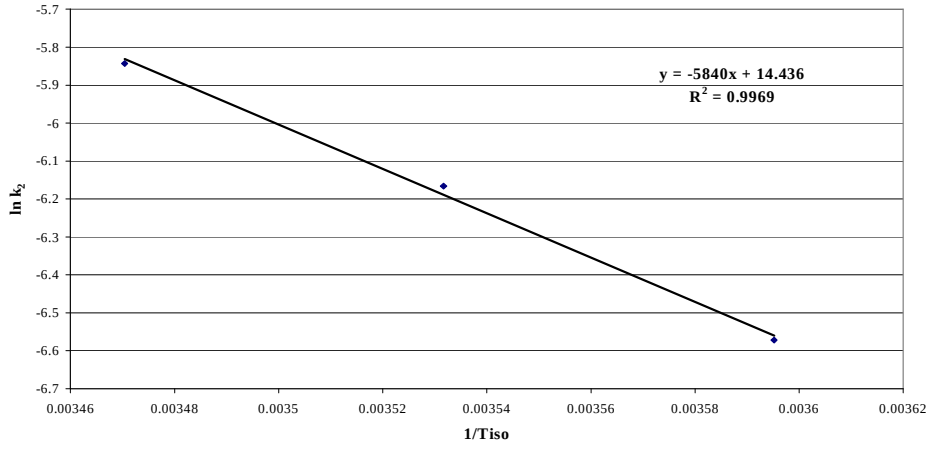


Figure 6.11: Arrhenius plot for k_2

The activation temperature for the first part of the synthesis reaction, i.e. the production of the intermediate was determined to E/R= 5840K. If this value is now compared to the activation temperature of E/R= 4483K determined with the first method in chapter 6.1., they at least are of the same magnitude. The values can be well compared this way, as in the first method of determining the kinetic parameters of the synthesis reaction, only the very first part of the heat release curve was evaluated, where it is assumed that the decomposition and the reaction from the intermediate to the product do not take place yet.

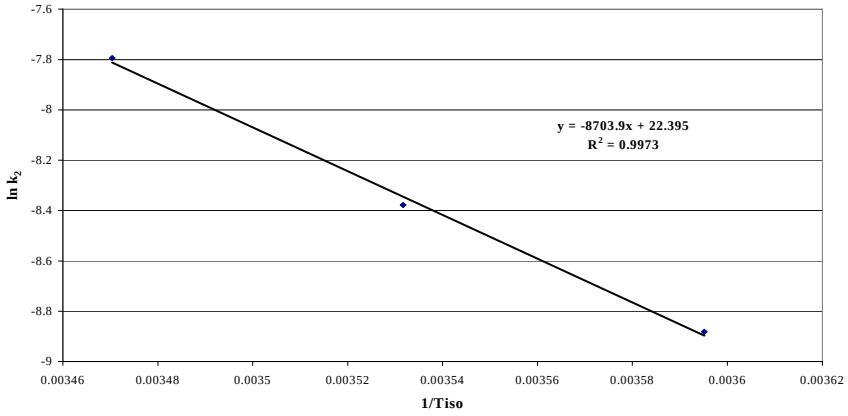


Figure 6.12: Arrhenius plot for k_3

The activation temperature for the second part of the synthesis reaction, i.e. the production of the di-peroxide, was determined to E/R= 8704K. This value is now compared to the activation temperature of E/R= 8531K determined with the second method in chapter 6.1. They are again in the same range. This comparison is possible as in the second method of determining the kinetic parameters of the synthesis reaction, the part of the reaction was evaluated, where the decomposition already takes place as well. But in this part, the synthesis reaction is dominated by the reaction of the intermediate with a hydroperoxide to the product di-peroxide. Therefore the first part of the synthesis reaction can be neglected and the parameters, which were determined in two different ways, can be compared. In the following table 6.5 all determined kinetic parameters are summarized.

Table 6.5: Kinetic parameters

Reaction	E/R [K]	k_∞
Decomposition of the hydroperoxide	13717	$2.874 \cdot 10^{14} l^{4.6}/(mole^{4.6} \cdot s)$
Formation of the intermediate	5840	$1.86 \cdot 10^{6} l^{2}/(mole^{2} \cdot s)$
Formation of the di-peroxide	8704	$5.32 \cdot 10^{9} l^{2}/(mole^{2} \cdot s)$

With these determined values the corresponding experiments in the RC1*e* at 5°C, 10°C and 15°C were simulated again and gave good results, in the following figures 6.13, 6.14 the experiment at 10°C is shown, first the heat curves and then the amount of substance of educts and products.

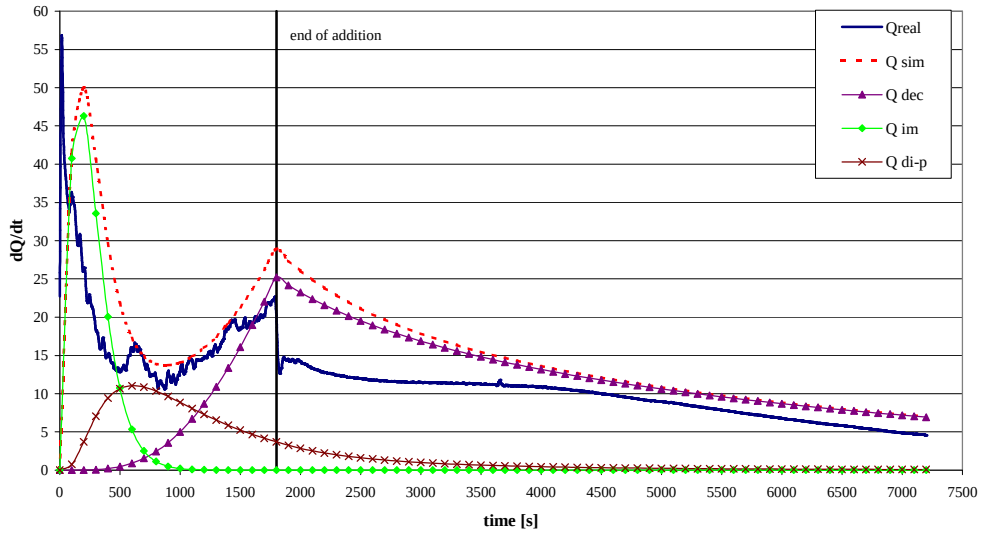


Figure 6.13: Simulation of the experiment at 10°C with the second model, fitted parameters

The simulation of the experiment at 10°C verifies the result of the determined kinetic parameters, the simulated and measured curve agree quite well, although the simulated heat release rate is still higher than the measured one. As this time the temperature is higher and therefore the decomposition of the peroxide rises, the difference of the simulated and measured released heat in the end of the reaction is not that high any more. In the following diagram the corresponding amount of educts and products is shown.

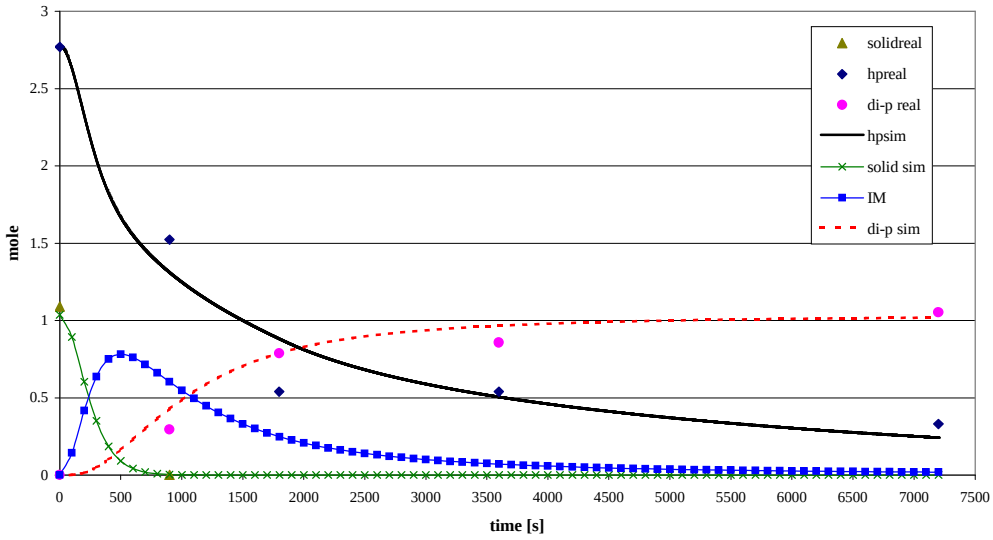


Figure 6.14: Simulation at 10°C, amount of educts and products

It can be well observed that the measured and simulated values fit quite well, and therefore prove the model as already did the heat curves.

The results of experiment and simulation at 15°C are shown in the following figure 6.15.

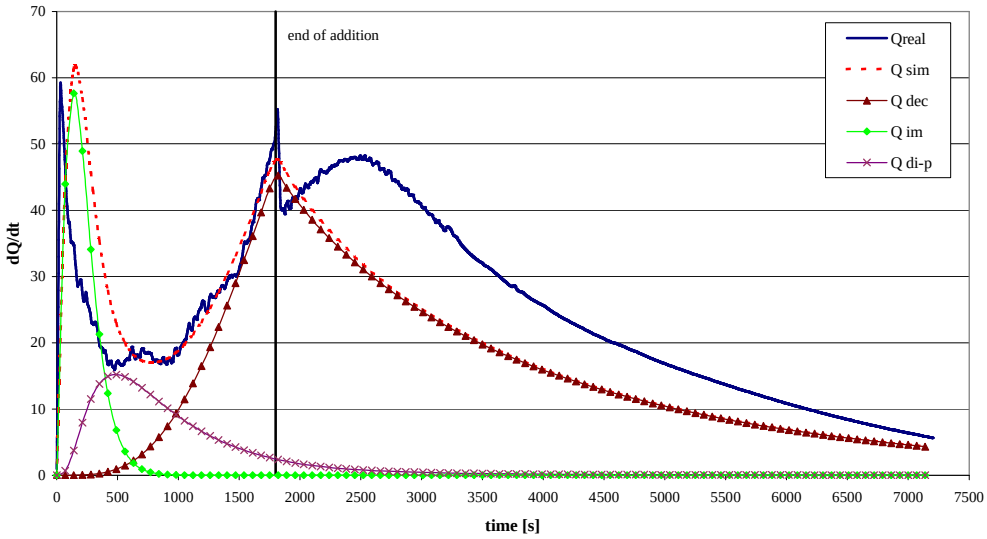


Figure 6.15: Simulation at 15°C, heat release rates

As in the other diagrams, the simulated and measured curves agree quite well, with the higher temperature the decomposition gets more influence on the reaction, as the activation temperature of the decomposition is with 13700K much higher than the activation tempera-

tures of the synthesis with 8700K and 5800K. This time the simulated heat release rate after the end of the addition is smaller than the measured one. A reaction enthalpy of -186kJ was measured, while the simulated reaction enthalpy is only -145kJ. This might be caused by a higher decomposition of the hydroperoxide than simulated for one reason. This suggestion is enforced by the simulated and measured amount of hydroperoxide in the end of the reaction, which can be observed in the following figure 6.16. Another reason of the higher measured heat release rate might be an already started decomposition of the di-peroxide or the intermediate, which was neglected in the model.

In the following figure the amount of educts and products is shown over the reaction time.

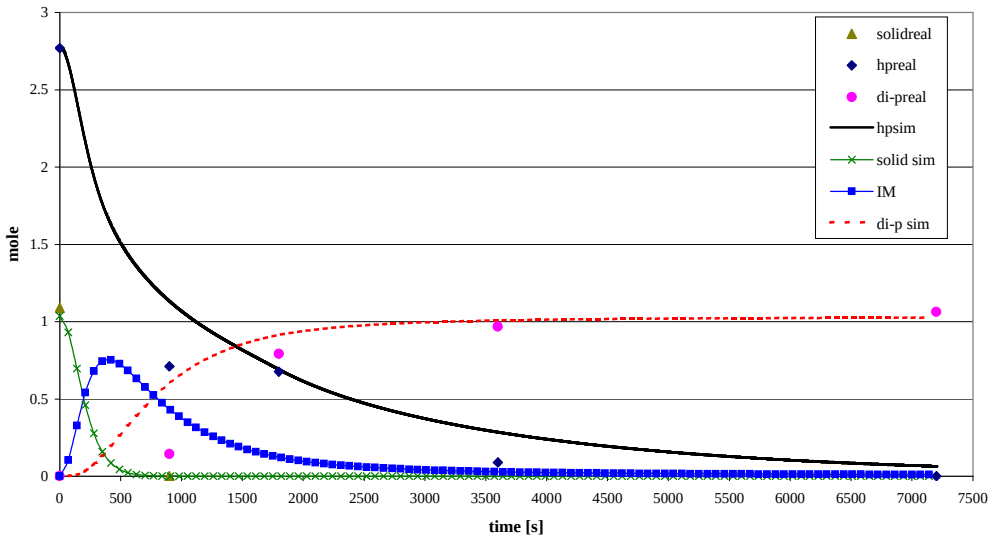


Figure 6.16: Simulation at 15°C, amount of educts and products

This time the simulated curves and measured points do not fit that well, but it can be well observed, that in the end of the reaction the simulated value for the hydroperoxide is still higher than the measured, which shows that the decomposition in reality might have been higher than in the simulation.

In the following figure an example is shown for an experiment at 20°C.

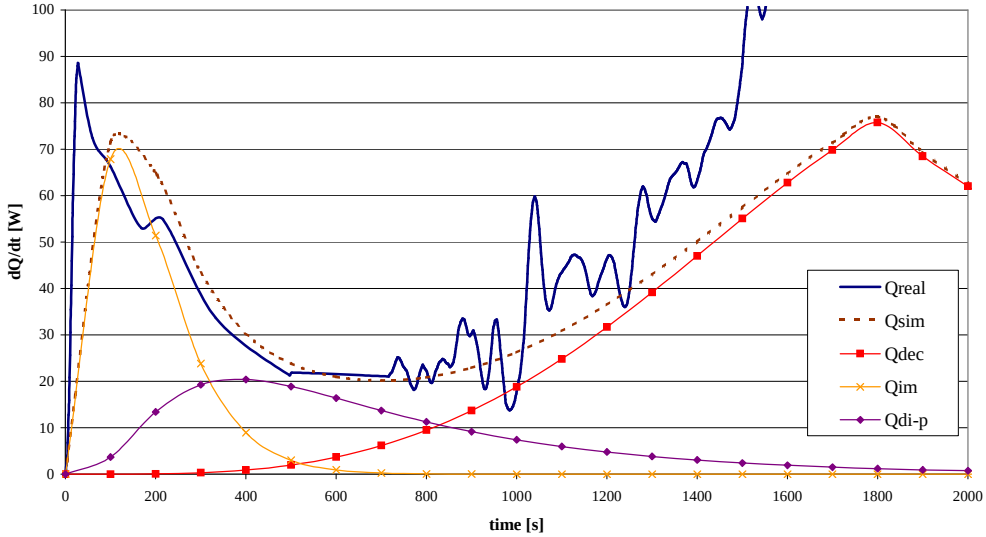


Figure 6.17: Experiment at 20°C, simulation and measured curve

This curve shows a runaway in the reaction calorimeter RC1*e* which was later stopped with the addition of chilled water. The simulation fit quite well with the measured data until approximately 1400s. Then the measured heat release rate starts to runaway, while the simulated curve reaches again with the end of the addition at 1800s its maximum and then decreases again. Obviously in the measured experiment not only the hydroperoxide but also the resting intermediate and the di-peroxide decomposed at the higher temperature. This was neglected in the model, but should always be kept in mind when operating this reaction. At higher temperatures also the di-peroxide can start to decompose.

Chapter 7:

Discussion

7.1. Introduction

In this chapter the results presented in chapters 5 and 6 will be discussed. The method of determining the hazardous potential of a planned process following the German regulation TRAS 410 will again be used here. Based on the explanation of the TRAS 410 in chapter 3 the analysed synthesis will be discussed concerning its safety. Then, discussions on the application of safety criteria, the reaction kinetics and the simulations will follow. In the end recommendations regarding the scale-up of the synthesis will be given and discussed.

7.2. Applying the TRAS 410-procedure to the analysed reaction

The analysed reaction system caused several problems at various steps of the analysis as was already shown in earlier chapters. The procedure will be explained stepwise. The first part of the TRAS 410 can be seen in the figure 7.1 below.

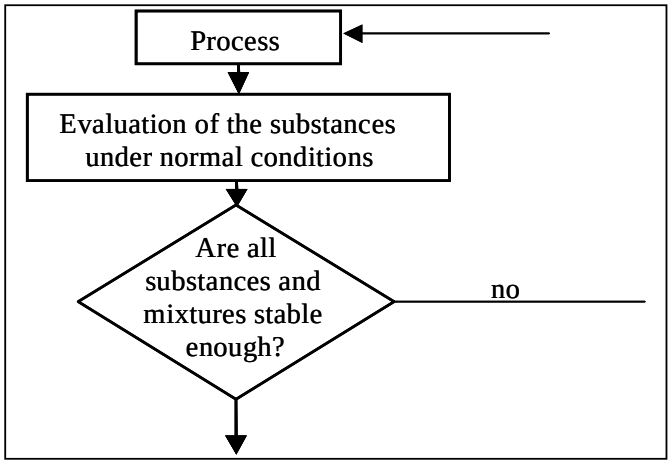


Figure 7.1: First part of TRAS 410

These first analyses of the substances can be performed with the help of DSC, TS^U and TEVT. It was found for the investigated system that for normal conditions all substances are stable enough (see chapter 5.1.). Further, the decomposition reactions of the substances were also analysed. Problems in analysing the substances in this step were found in the very fast and highly exothermic reaction of the peroxides. Due to this behaviour isothermal measurements in the DSC could not successfully be performed for the hydroperoxide. Therefore a Time to Maximum Rate (TMR) could not be calculated exactly in the case of the hydroperoxide. Experiments were performed in the TEVT to analyse the substances on explosiveness. The hydroperoxide and the di-peroxide did not show great risks concerning explosiveness in the TEVT, but a highly exothermic decomposition in the DSC, as well as the mixture of the intermediate with di-peroxide. Comparing all substances and mixtures, the hydroperoxide has the highest hazard potential. The maximum process temperature according to the 100K-rule is 5°C for the hydroperoxide. This safety limit, which is valid for all substances as the hydroperoxide has the highest hazard potential, is already very low regarding possible process temperatures, which is a first sign that the process will have to be changed.

After the evaluation of the substances the reaction itself has to be investigated as can be seen in the following figure 7.2.

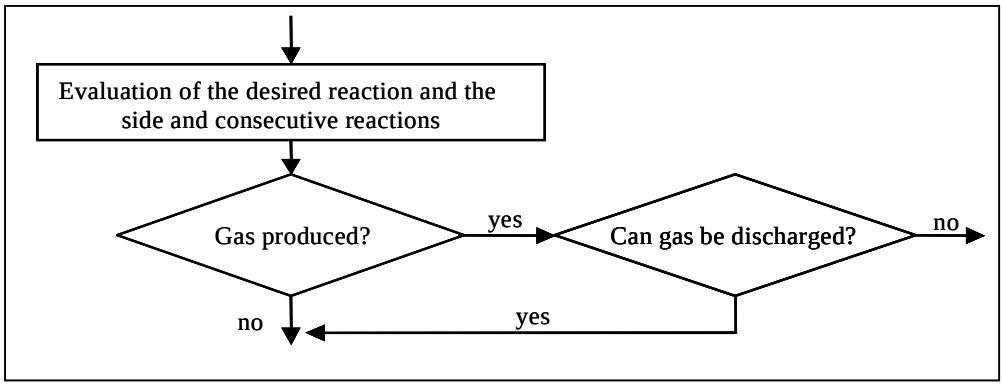


Figure 7.2: Second part of TRAS 410

The reaction was first tested in the mini-laboratory reactor and later slightly modified as well in the RC1*e*. The results were presented in chapters 5.2. and 5.3. It was found that under normal conditions there should not be a development of gas, because during the synthesis reaction only di-peroxide and water is produced. Only if part of the peroxides start to

decompose, gas is produced. It is therefore advisable to operate the reaction in an quasi open system (due to the necessary explosion protection, it cannot be totally open) that the possibly produced gas can always be discharged. Further it has to be considered that the onset-temperature of the decomposition of the hydroperoxide is lowered by the catalyst. The experiment in the RC1*e* at 15°C already showed a decomposition of the hydroperoxide. It might therefore be advisable to change the process to a lower process temperature to avoid any decomposition and keep the system stable at the synthesis reaction.

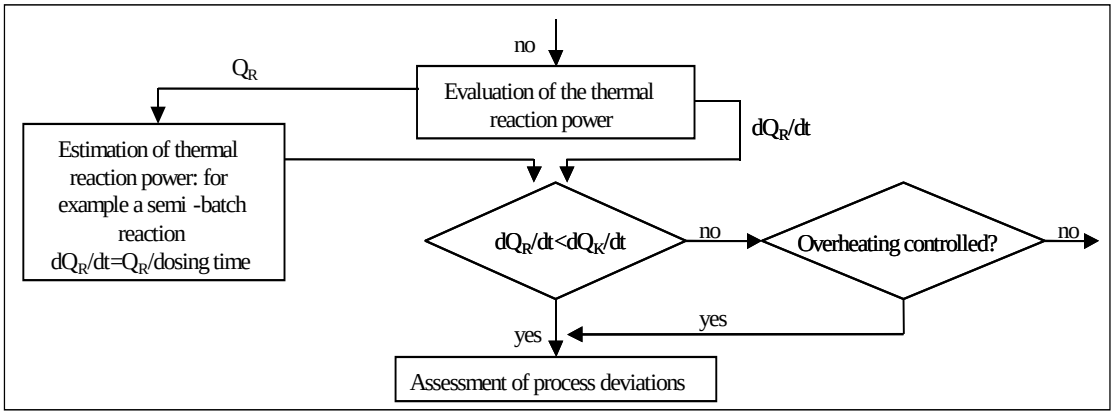


Figure 7.3: Third part of TRAS 410

The results concerning the evaluation of the thermal reaction power in a third step are presented in detail in chapter 5.2. and 5.3. In the following table 7.1 the maximum heat release rate of the reaction (dQ_R/dt) and the maximum cooling capacity (dQ_C/dt) for experiments at three different temperature are shown.

Table 7.1: dQ_R/dt and dQ_C/dt at experiments in the RC1*e*

T_{iso} of experiment [°C]	max dQ_R/dt [W]	max dQ_C/dt [W]
5	38.6	46.6
15	59.3	54.5
20	595	243

It can be well observed in table 7.1 that only at an isothermal temperature of 5°C the released heat from the reaction can safely be removed, already at 15°C the cooling capacity is not totally sufficient and at 20°C a thermal runaway is expected and indeed occurred in the experiment.

The influence of different parameters on the reaction was analysed in the mini-laboratory reactor and it was evaluated that it would be most sensible to operate the process with the solid of a small particle size (<0.5mm) and an addition time of at least 30min for a 1l-scale like the RC1*e*. For usual semi-batch reactions, where one of the reaction partners is added, the accumulation is an important factor for the safety, as an accumulation will delay the reaction, which later starts with all accumulated reactant and cannot be controlled by the addition any more. In the presented case the catalyst is added instead of a reactant. Therefore the problem of a too fast addition has to be observed in a slightly different way. As the catalyst is no reactant, its fast addition cannot cause an accumulation. But a too fast addition will set free a great amount of dissolution heat and the temperature will rise fast. With the higher temperature and the already added catalyst the decomposition of the hydroperoxide will be favoured instead of the synthesis reaction and a thermal runaway will therefore occur. The addition has therefore to be slow enough to avoid a too great heat production and to always ensure that the synthesis reaction is favoured. In the experiments in the RC1*e* it was further found that a low process temperature and slight dilution of 12-15% water in the hydroperoxide already helps to avoid a decomposition of the peroxides and therefore a thermal runaway. Under normal conditions there should not be any problem in the RC1*e* with the produced heat and cooling capacity. Only for the decomposition the cooling capacity might not be sufficient, depending on the process temperature and therefore the amount of peroxide decomposed. It was found in the experiments in the RC1*e* that already a process temperature of 15°C is quite critical while an experiment at 20°C ended up in a thermal runaway. The dilution with water of the system and operating it in an open way would be in this case very helpful. Then the temperature cannot rise infinitely in case of a starting thermal runaway but stops at 100°C due to the evaporation of the water, which cools off the system. This of course implies that all released heat is removed by the evaporation. The mass of the evaporating solvent for the removal of a distinct amount of energy can be calculated as follows:

$$m_{vap} = \frac{Q_r \cdot m_r}{\Delta H_v} \tag{7.1}$$

With m_{vap} [kg] as the mass of the evaporated solvent, Q_r [J/kg] the reaction heat, m_r [kg] the reaction mass and Δh_v [J/kg] the evaporation enthalpy. With an Δh_v for water at 100°C of approximately 2250kJ/kg [Stephan] the necessary amount of water for the cooling of the reaction system (for the experiment at an isothermal temperature of 15°C) can be approximated to 82g. As approximately 210g of water were in the RC1*e*, the evaporation would be sufficient to prevent a runaway. But for this case only the released heat measured by the RC1e during the experiment was considered, not the possible released heat by a complete decomposition of the hydroperoxide. For a cooling of this decomposition an amount of water of at least 255g were calculated. Therefore for a completely inherent safe system the dilution with water has to be increased, with the negative consequences of a decreasing productivity.

The evaluation of the process under normal operating conditions already showed that the synthesis cannot be performed as planned. It is suggested to lower the process temperature as much as possible, but at least to 5°C. The experiments in the RC1*e*, see also chapter 5.2., showed that this will not even have a too great influence on the productivity. This lower temperature prevents the decomposition of the peroxides and therefore enhances the safety of the system. Also a slight dilution with water would be helpful to prevent a thermal runaway.

After the evaluation of the process under normal conditions, possible process deviations have to be analysed.

Concerning the assessment of the possible process deviations for the analysed reaction it should be thought of all possible cases. For a complete discussion of all these deviations also information on the technical and organisational surroundings of the planned process are needed. As the plant conditions are unknown until now, not all possible deviations can be considered.

For an estimation of the possible consequences of process deviations, a worst case scenario has to be analysed. This worst case is for an exothermic reaction usually the adiabatic case, where no heat is exchanged with the environment. The presented synthesis reaction was analysed in the adiabatic batch reactor ADC II to get an idea on its adiabatic behaviour. The results of these adiabatic experiments are found in chapter 5.3.

In the following there are some deviations of the process and their possible consequences shown.

Deviations and their consequences:

- *The addition of the catalyst is faster than usually:* Reaction rate will increase and therefore the reaction temperature as well. With the higher temperature the decomposition of the hydroperoxide will increase, overheating will possibly not be controllable.
- *The addition of the catalyst is slower than usually:* Reaction is also slower, but no negative consequences concerning the safety will occur.
- *The reaction temperature is higher than usually:* Reaction rate will increase and therefore the reaction temperature and the decomposition of the hydroperoxide will increase as well, overheating might not be controllable.
- *The reaction temperature is lower than usually:* Reaction rate will decrease a little and the productivity might sink. As no accumulation was observed in a temperature range of 5-20°C, no negative consequences concerning the safety will occur.
- *No solid was added:* The addition of the catalyst will lower the onset-temperature of the decomposition of the hydroperoxide, a thermal runaway is well possible.
- *The concentration of the hydroperoxide is higher than usually:* A higher amount of hydroperoxide is available for the decomposition and the solution is more concentrated, reaction speed will increase and more hydroperoxide will decompose, a thermal runaway will occur.

- *The concentration of the hydroperoxide is lower than usually:* A lower amount of hydroperoxide is available for the decomposition and the solution is less concentrated, the productivity might decrease but safety of the system increases due to the dilution. As the catalyst is added and not a reactant, no further accumulation and therefore no safety problems can occur.
- *No stirring:* The cooling gets inefficient as the mass inside the reactor is not well mixed any more. On the other hand the added catalyst is not mixed either, which is necessary for the reaction in the heterogeneous system. But it is still possible that the hydroperoxide starts to decompose at the point where the catalyst is added and therefore heats up the complete system, which might end up in a runaway.
- *No cooling:* With a cooling failure the heat cannot be transported and the reactor will heat up adiabatically rapidly. A thermal runaway will occur.

These presented deviations and possible consequences already show that a very good emergency system is needed to perform the process safely. This implies for example an automatic stop of the addition of the catalyst in case of a cooling or stirring failure. Further there have to be an emergency cooling and an emergency quenching system, which means the immediate addition of chilled water to prevent a thermal runaway. It is very much advisable to operate in an open system to avoid any rise in pressure and to dilute the system with water to get an inherent safety margin at 100°C due to the evaporation of the water, if the condensing and reflux system is well designed.

7.3. Application of safety criteria

It is always helpful to apply general safety criteria to a process to ensure that it will at any time operate in a safe way. Steinbach [Steinbach 3] presented safety criteria for the four reactor types BR, SBR, PFTR and CSTR. The safety criterion for the isothermal SBR for normal conditions is: Da (T_{iso}) ≥ 100. Following Steinbach again, another possibility for a recommendation on safety for an isothermal semi-batch-reactor is applying the safety criterion for the isoperibolic semi-batch reactor with the minimum cooling temperature as the characteristic temperature, which is defined as follows:

$$\frac{1.45 \cdot Da(T_{c,\,min})}{\frac{\varepsilon}{1+\varepsilon} + St} \geq 1 \tag{7.2}$$

But it has to be emphasized, that this is only a recommendation and not a yes/no criterion for the safety of an isothermal semi-batch reactor.

Unfortunately it is not possible to apply these safety criteria to the analysed process because they are meant for homogeneous reactions (of mostly second order) and not for consecutive or parallel reactions. In a reaction system where more than one reaction takes place, it is impossible to calculate one Damköhler number. Each side reaction has its own Damköhler number and therefore these criteria are not applicable in the classical way. Nevertheless, as these safety criteria are often used and normally easy to apply, attempts were made to apply them to the analysed process. The experiment in the RC1*e* at 5°C was chosen as an example and the corresponding Stanton number could then be calculated to:

$$St = \frac{U \cdot A \cdot t_{char}}{V \cdot \rho \cdot c_p} = 6.3 \tag{7.3}$$

Now the Damköhler number, which is defined as follows:

$$Da = \frac{(-\nu_a) \cdot r_0 \cdot t_{char}}{c_{a0}} \tag{7.4}$$

has to be calculated. As already mentioned, for each reaction one Damköhler number has to be calculated and therefore for the presented reaction system, three Damköhler numbers have to be calculated. It was tried to form one Damköhler number which would at least approximate the complete reaction system, but no reasonable data were obtained. It must be stated that an overall Damköhler number would neglect the different temperature dependencies of the side reactions, which would simplify the model too much.

Making the assumption of the border case that no decomposition takes place and the hydroperoxide completely reacts with the solid to the intermediate, the Damköhler number for the synthesis reaction to the intermediate can be calculated. Taking the experiment in the RC1*e* at 5°C as an example, the Damköhler number can be determined to Da = 31.6, which is still too low for a safe isothermal semi-batch-reactor. For the application of the

second, originally isoperibolic safety criterion a Damköhler number of 16.1 is calculated and the criterion gives a value of 3.5, which means that in this case the process would possibly be safe. This corresponds very well with the results observed during the experiments in the RC1*e*, as there the process was safe when it was not dominated by the decomposition.

The Damköhler number was also calculated for the second part of the synthesis reaction, the formation of the di-peroxide out of the intermediate. But this case is only theoretical, it cannot even represent a border case of the reality, as the reaction always has to start with the formation of the intermediate. The Damköhler number can be calculated to $Da(T_{iso}) = 3.1$ and the first safety criterion is then not fulfilled. For the application of the second, originally isoperibolic safety criterion a Damköhler number of 1.1 is calculated, the criterion gives a value of 0.24 and is therefore not fulfilled. During the experiments no problems were observed for the final reaction from the intermediate to the di-peroxide, but it has to be kept in mind, that the analysed case here is very theoretical.

In the following table 7.2 the resulting Damköhler numbers and the application of the safety criterion for the two synthesis reactions at different temperatures can be seen.

Table 7.2: Damköhler numbers and safety criteria for the synthesis reaction at different temperatures

reaction	T [°C]	Da (T_{iso})	Da ($T_{c,\,min}$)	safety criterion
formation of intermediate	5	31.6	16.1	3.5
formation of intermediate	10	45.8	23.9	5.2
formation of intermediate	15	65.5	27.6	6.0
formation of intermediate	20	92.6	45.8	10.0
formation of di-peroxide	5	3.1	1.1	0.24
formation of di-peroxide	10	5.3	2.0	0.44
formation of di-peroxide	15	9.0	2.5	0.54
formation of di-peroxide	20	15.1	5.3	1.16

Regarding only the two consecutive reactions of the synthesis reaction it seems reasonable to operate the process at a temperature of 20°C, as then the safety criterion is fulfilled for both reactions and the Damköhler number of the isothermal temperature for the formation of the intermediate is with 92.6 at least close to the desired 100. But as already discussed in detail in earlier chapters, there is a parallel reaction, the decomposition of the hydroperox-

ide. If the reaction rates of the three side reactions at different temperatures are regarded, it is obvious that the process should be operated at low temperatures. In the following figure 7.4 the initial rates of reaction of the three reactions at different temperatures can be seen.

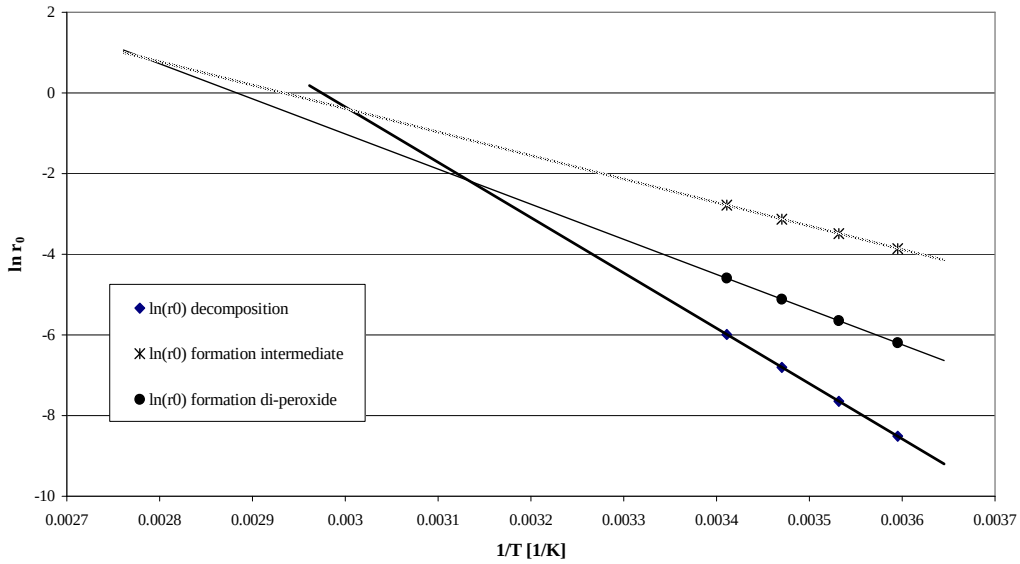


Figure 7.4: Initial rates of reaction of the three reactions at different temperatures

Regarding the diagram in figure 7.4 it can be stated that at a temperature of 20°C, which is equivalent to an 1/T of 0.0034 [1/K], the reaction rates of the decomposition and the synthesis reaction are too close together for a safe process. At a temperature of 44°C ($1/T \approx 0.00315K^{-1}$) the decomposition reaction is already as fast as the formation of the di-peroxide, at a temperature of 58°C ($1/T \approx 0.003K^{-1}$) the decomposition reaction is as fast as the formation of the intermediate. This case has to be avoided, the decomposition reaction should always have only a minor influence on the process. Therefore lower temperatures of 5°C (or below) have to be favoured, where the difference between the rates of reaction of the synthesis reaction and the decomposition is as large as possible. The reaction rate of the synthesis has to be always higher than the decomposition.

Although the decomposition reaction is not the desired reaction and the process is therefore not designed for it, the safety criteria and Damköhler numbers for the decomposition reaction were calculated for different temperatures and can be seen in the following table 7.3.

Table 7.3: Damköhler numbers and safety criteria for the decomposition at different temperatures

T [°C]	Da (T_{iso})	Da ($T_{k,\ min}$)	safety criterion
5	0.12	0.074	0.016
10	0.28	0.187	0.041
15	0.64	0.262	0.057
20	1.45	0.862	0.188

The table 7.3 shows, as expected, that the decomposition reaction does not fulfil any safety criteria. As already determined, the decomposition is critical for the process and has to be avoided.

After the calculation of Da (T_{iso}) for the decomposition reaction, another diagram can be used to determine the safe temperature range for the process. As the Damköhler number is an indicator for the reaction rate and as it was already stated that the synthesis reaction should always be faster than the decomposition reaction, the following condition should always be fulfilled: $Da(T_{iso})/Da(T_{iso})_{dec} > 1$. In the following figure 7.5 this condition and the application of safety criterion (equation 7.2) for the two synthesis reactions are shown.

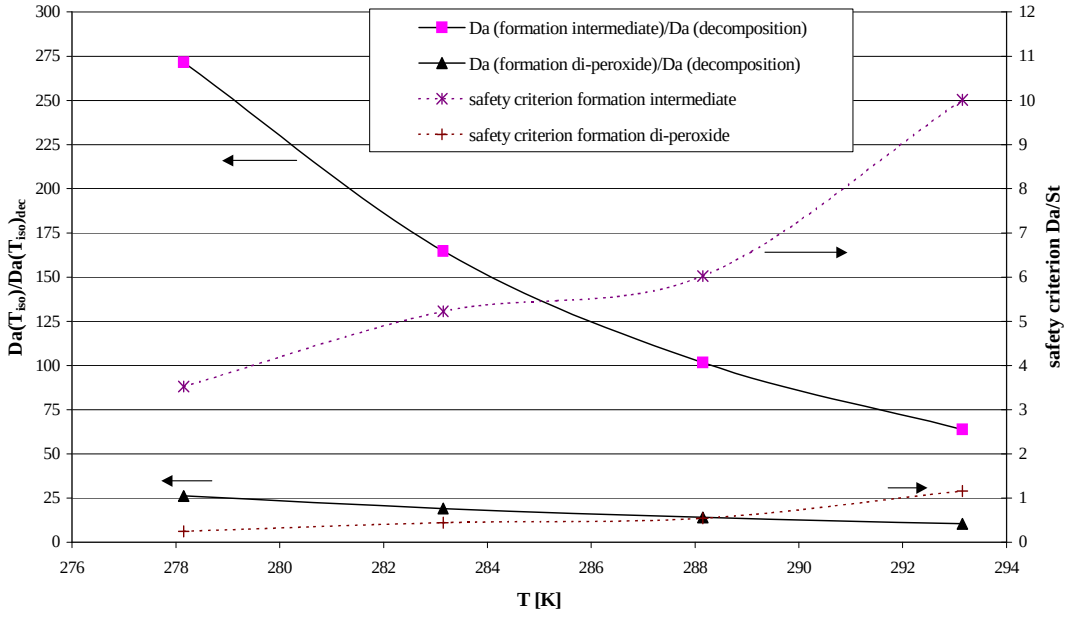


Figure 7.5: Application of the safety criterion on the two synthesis reactions

From the figure 7.5 the safety criteria for the two synthesis reactions can be observed and again on the first sight it seems that a temperature of 20°C (293K) would ensure a safe process as then the safety criterion for each synthesis reaction is fulfilled. But again it has to be kept in mind that during the calculation of the safety criteria the decomposition reaction was neglected, a fact which does not represent the reality. The factor $Da(T_{iso})/Da(T_{iso})_{dec}$ is then regarded. It should always be greater 1 to ensure that not the decomposition reaction but the synthesis dominates the process. From the diagram it can be seen, that the factor is always greater than 1 for the formation of the intermediate and for the formation of the di-peroxide. But the factor has to be as great as possible for a safe process. As it is increasing with lower temperatures, it is recommended to operate at a maximum temperature of 5°C (278K) to ensure a safe process.

Finally it can be stated that a method to apply the complete process to this safety criterion could not be found, but for the presented case it was found to be helpful to apply the criterion, originally meant for the isoperibolic semi-batch reactor, to the two synthesis reactions. With evaluations of the initial rate of reaction for the decomposition and the two synthesis reactions as well as the calculation of the factor $Da(T_{iso})/Da(T_{iso})_{dec}$ indications on critical and uncritical temperature ranges for the concerned process can be given.

Concerning the analysed peroxide synthesis it must always be remembered, that it is not a semi-batch reaction in the classical sense. This is due to the fact that not the second reaction partner is added, but the catalyst, which is not consumed by the reaction, but only slightly diluted by the formed water. This point complicates the application of safety criteria a lot. It is therefore almost impossible to apply the well approved safety criteria on this peroxide synthesis, but at least the criterion for the isoperibolic semi-batch reactor could be applied to the synthesis reactions and with a maximum temperature of 5°C a recommendation on a safe temperature range could be given.

It was also tried to applicate safety criteria of other authors like those found by Zaldivar and others [Zaldivar 2]. Their safety criterion for runaway limits in chemical reactors is: div =0. It says that the process is in a runaway situation when the divergence of the system becomes positive (div>0). Zaldivar [Zaldivar 2] defines the divergence as „a scalar quantity defined at each point as the sum of the partial derivatives of the mass and energy balances

with respect to the corresponding state variables, temperature and conversion“. According to the authors this criterion is also applicable for consecutive reactions, but until now no solution was found for a system with three side reactions, two consecutive and one parallel. Therefore this safety criterion might as well be used but was not applied.

Other safety criteria were shown by Balakotaiah [Balakotaiah 1], [Balakotaiah 2]. But although safety criteria for catalytic reactions are presented there, they cannot be used for the concerning reaction system, as the safety criteria by Balakotaiah and others [Balakotaiah 2] are meant for a solid catalyst, not for an added liquid one.

These few examples show that it can therefore be stated that up to now there is no suitable safety criterion which can easily be applied to such a complex reaction system. Although it must be stated that the first discussed safety criterion developed by Steinbach [Steinbach 3], originally meant for isoperibolic semi-batch reactions, could at least give good indications on the hazard potential of the reactions and a recommendation on a safe temperature range. The parameters for a safe operation of the reaction system has to be determined with the help of the scheme of the TRAS 410 and experiments and their corresponding simulation.

7.4. Reaction kinetics

There are already good and well approved methods to determine the reaction kinetics for a homogeneous reaction in a batch reactor. One example is the „isothermal equivalent reaction time method“, which was developed at the Technical University Berlin by Hugo et al. It is well described in [Hugo 2] and will therefore not be explained in detail here. This method is meant for batch reactions and makes it possible to evaluate simultaneously experiments at different temperatures, provided the experiments were performed in batch-mode with equivalent initial concentrations. The method can be well applied with the help of the software qtherk and qkin [Leonhardt]. One disadvantage of this method is the fact that until now it was restricted to experiments in the batch reactor.
Bundschuh [Bundschuh] could recently show that the „isothermal equivalent reaction time method“ can also be used for semi-batch reactors by transforming the measured semi-batch

data into a „pseudo“-batch mode. Then the „isothermal equivalent reaction time method“ can be applied, and therefore the software qtherk and qkin can also be used.
This method was not expected to work with the analysed reaction system, because the data from the semi-batch experiments are compressed to a very fast „pseudo“-batch experiment. This compression leads to a multiplication of errors and in the presented case to „pseudo“-batch data which could not be evaluated. Furthermore, assumptions had to be made to be able to transform the semi-batch reaction into a „pseudo“-batch reaction, like the existence of only one reaction and a formal kinetics of second order. Both assumptions are not fulfilled for the presented, complex peroxide synthesis. It was still tried for the presented synthesis to transform the semi-batch experiments into a „pseudo“-batch mode and then apply the „isothermal equivalent reaction time method“ with the software qtherk and qkin. But as already expected, no reasonable data were obtained.

Starting the experiments it was assumed that there will be only a single reaction, the formation of a di-peroxide out of a hydroperoxide and a solid. It was known that this reaction will proceed in a two-step mechanism, first the reaction from the solid together with one hydroperoxide to an intermediate and then the reaction of the intermediate with a hydroperoxide to the di-peroxide. But it was assumed that this intermediate will disappear that fast, that the two reactions can be described with one formal kinetic rate law (Bodenstein principle).

The results from the experiments in the RC1*e* showed that none of the two assumptions were true. Analysis in the HPLC of samples taken during the experiment showed the existence of an intermediate, which already lead to the speculation that the consecutive reaction of the intermediate to the di-peroxide cannot be neglected. Furthermore there were different enthalpies for experiments at different temperatures detected, which is a strong sign for a second, parallel, reaction which also takes place. These results explain well, why the program qtherk, qkin did not give good results, as this is meant for homogeneous and single reactions.

The formal kinetic rate law of the reaction system therefore had to be changed, it was then assumed that there are two consecutive reactions for the formation of the di-peroxide and parallel there is the decomposition of the hydroperoxide. The rate determining step is

hereby the reaction to the intermediate under the presence of the catalyst. Therefore the synthesis reaction is controlled by the addition of the catalyst, as without, no reaction can be observed. The reactions for the formation of the di-peroxide can be both described as of „pseudo“-third order with the solid as the first, the hydroperoxide as the second and the catalyst as the third reaction partner, this is equivalent for the reaction from the intermediate to the di-peroxide.

The formal kinetics of the decomposition of the hydroperoxide were quite complex. All experiments showed that the concentration of the catalyst has a strong influence on the reaction. Various attempts were made to include this strong influence of the catalyst in the most realistic way.

First a common reaction kinetics for catalysis following the scheme below was tried [Hugo 1]:

$$\begin{aligned} A + cat &\xrightarrow{k_1} Acat \\ Acat &\xrightarrow{k_2} A + cat \\ Acat + A &\xrightarrow{k_3} C + cat \end{aligned}$$

and the following reaction rate resulted:

$$r = \frac{k_1 \cdot k_3 \cdot c_a^2 \cdot c_{cat}}{k_2 + k_3 \cdot c_a} = \frac{k_1 \cdot c_a \cdot c_{cat}}{1 + \frac{k_2}{k_3 \cdot c_a}} \tag{7.5}$$

If it is now assumed that $k_2/(k_3 \cdot c_a) \approx 1$ the reaction rate r for the decomposition is as follows:

$$r = k^* \cdot c_a \cdot c_{cat} \tag{7.6}$$

Finally a formal kinetic rate law as the following was tested:

$$r = k \cdot c_a \cdot c_{cat}^n \tag{7.7}$$

with n as the „order“ of the concentration of the catalyst. This is unusual to describe a catalytic decomposition and not correct in a sense of a formally „right“ reaction kinetic in a molecular sense. But with n = 4.6 the reaction process can be described quite well, as was

shown in chapter 5.4. and therefore it seems practicable to operate with the following presented model, with one parallel decomposition of the hydroperoxide and two consecutive reactions for the formation of the di-peroxide.

I. decomposition of the hydroperoxide:

1 hydroperoxide + catalyst → 1 decomposition product + catalyst

II. formation of the intermediate:

1 solid + 1 hydroperoxide + catalyst → 1 intermediate + 1 water + catalyst

III. formation of the di-peroxide:

1 intermediate + 1 hydroperoxide + catalyst → 1 di-peroxide + 1 water + catalyst

In general it is difficult to determine reaction kinetics of two parallel reactions. Sempere and others [Sempere] determined the reaction kinetics of the N-oxidation of 2-methylpyridine with the help of hydrogen peroxide and of the parallel decomposition of the hydrogen peroxide in the RC1*e*. In that case the progress of the decomposition reaction could be measured with the help of the oxygen effluent, as hydrogen peroxide decomposes to water and oxygen. For the analysed process in the work presented it was not possible to determine exactly the progress of the decomposition of the hydroperoxide. Therefore the amount of decomposed hydroperoxide was calculated with the help of the mass balances, which is of course not as exact as a continuous measurement of the decomposition. Nevertheless the simulated data gave reasonable results.

7.5. Simulations

A model was put up to re-simulate the experiments in the RC1*e*. Besides the reaction kinetics of the three, consecutive and parallel, reactions, which are meanwhile known, there is the mass transfer between the different phases, as it is a heterogeneous system. As the hydroperoxide is organic and the catalyst inorganic, there is already a liquid-liquid system. As the second reaction partner is a solid, in the beginning there is a solid-liquid-liquid heterogeneous system. Usually for the simulation of a heterogeneous system the mass transfer between the different phases is important and has to be considered. It is always advisable to

keep the kinetic model as simple as possible but as complex as necessary. For that reason the mass transfer between the solid and the organic liquid was neglected, as the substances are always well stirred and therefore well mixed and the solid reacts very fast with the hydroperoxide that after 10-15min no solid is found any more. The two liquid phases only become important with time, as the inorganic catalyst is added and the water is formed with the synthesis reaction and therefore the inorganic phase in the beginning is rather small. This mass transfer between the two liquid phases was also not considered directly in the model as the inorganic catalyst is added to a well mixed system, and the reaction system is not controlled by the mass transfer but by the addition. Therefore this mass transfer is considered in the model indirectly with the addition of the catalyst. Further the dissolution heat of the catalyst was also not considered directly but indirectly in the reaction enthalpies. The catalyst itself is also diluted slightly by time as the synthesis reaction produces water. As this dilution is rather small (in the analysed system with approximately 200g solid, 340g hydroperoxide and 500g catalyst, only 40g of water is produced), this effect is also neglected.

But a special attention was paid to the reaction system itself. It was found from several simulation efforts that it is very important not to neglect the consecutive synthesis or even the parallel decomposition reaction. The determination of their corresponding parameters was difficult, because not enough experimental data were available, for example the concentration of decomposed hydroperoxide with time. Those parameters were then defined iteratively with the help of the simulations. The formal kinetics for each side reaction were determined to:

I. decomposition of the hydroperoxide, $E/R = 1.37 \cdot 10^4 K$ and $k_\infty = 2.874 \cdot 10^{14} l^{4.6}/(mole^{4.6} \cdot s)$

$$r = k \cdot c_{hydroperoxide} \cdot c_{catalyst}^{4.6}$$

II. formation of the intermediate, $E/R = 5.8 \cdot 10^3 K$ and $k_\infty = 1.86 \cdot 10^6 l^2/(mole^2 \cdot s)$

$$r = k \cdot c_{hydroperoxide} \cdot c_{solid} \cdot c_{catalyst}$$

III. formation of the di-peroxide, $E/R = 8.7 \cdot 10^3 K$ and $k_\infty = 5.32 \cdot 10^9 l^2/(mole^2 \cdot s)$

$$r = k \cdot c_{intermediate} \cdot c_{hydroperoxide} \cdot c_{catalyst}$$

With the simulations a reasonable model resulted. It is considered that in the beginning of the reaction the rate determining step is the addition of the catalyst. Later, the system is not controlled by the addition as the accumulation is too high and the heat release rate does not decrease completely with the end of the addition. With the end of the addition the system is considered to be kinetic controlled as the reaction mass is always well mixed that the mass transfer can be neglected. The model was developed for a temperature range from 5°C-15°C and can be used for a prediction of the danger of a runaway at different conditions at least in the reaction calorimeter RC1*e*.

7.6. Recommendations on the scale-up of the synthesis

For a scale-up of a reaction it is always helpful to have general safety criteria to follow to ensure a safe process. As discussed in chapter 7.2. this is not possible for the presented peroxide synthesis. Therefore the scheme following the TRAS 410 has to be executed as described in chapter 7.1. This procedure and the results of the experiments in the RC1*e* lead to the perception that it is not possible to operate the process safely at a temperature of 15°C, due to the lower onset temperature of the decomposition of the hydroperoxide under the influence of the catalyst. Having applied the TRAS 410 to the reaction, a maximum temperature of 5°C is advisable. This maximum temperature resulted from the 100K-rule based on the decomposition of the hydroperoxide. As this maximum temperature was determined with the DSC and without the presence of the catalyst, the catalytic effect of it, a lower onset-temperature of the decomposition of the hydroperoxide, was not exactly considered. But as it is assumed that also the steel of the sample cells for the DSC measurements has a catalytic effect on the decomposition of the hydroperoxide and therefore also lowers the onset-temperature, this maximum temperature seems practicable. In fact, the experiment at 5°C in the RC1*e* showed that there was only little decomposition of the hydroperoxide in the end of the reaction, where the concentration of the catalyst has reached its maximum. The results of the experiments in the RC1*e* further showed that the production of the di-peroxide does not highly depend on the temperature, but on the addition of the catalyst. Therefore a lower temperature would not even cause a great decrease of productivity. At this point it has to be emphasized that up to now only experiments in the

RC1*e* at 1l-scale could be performed safely. In 1997 Nomen could show that already at this small scale large differences concerning the reaction behaviour and enthalpy are found when measured in different calorimeters as well as by different persons [Nomen 3]. Furthermore it was mentioned in this article, that steel might have a great catalytic effect on the reaction. As the presented reaction also shows a sensitivity to steel, it is important to start the next scale, the pilot scale, with precautions.

As also already mentioned the safety would increase as well with a dilution with water, as then with a high dilution the decomposition of the hydroperoxide is almost stopped due to the lower concentration of the catalyst, but unfortunately the production of the di-peroxide also decreases distinctly.

Another possibility to increase the safety would be a prolongation of the time of the addition. As the reaction is strongly dependent on the addition of the catalyst, it would slow down if the catalyst is added more slowly. This of course also implies that the process could be kept stable at the isothermal temperature in a better way, which again lowers the risk for a decomposition of the hydroperoxide, which is highly dependent on the temperature. But the production of the same amount of di-peroxide will of course take more time. In the following diagram 7.6 a simulation of an experiment in the RC1*e* at 5°C with an addition time of 1h instead of 30min is shown.

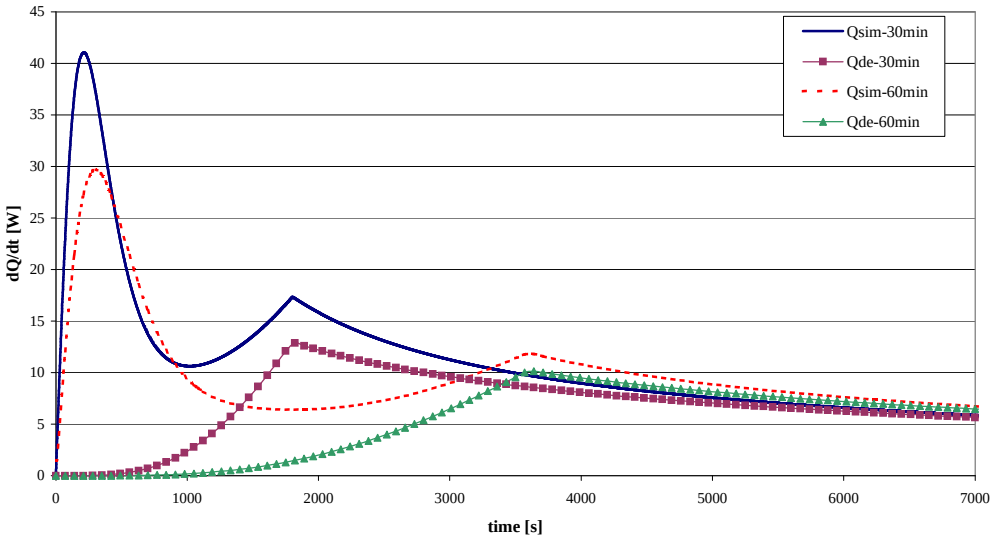


Figure 7.6: Comparison of heat production for an addition of 30min and 60min

It is clearly visible that the prolongation of the addition time results in a decrease of the maximum heat release rate and the decomposition of the hydroperoxide also starts later and with a lesser heat release rate. In the next figure 7.7 the amount of substances and the production of the di-peroxide are shown.

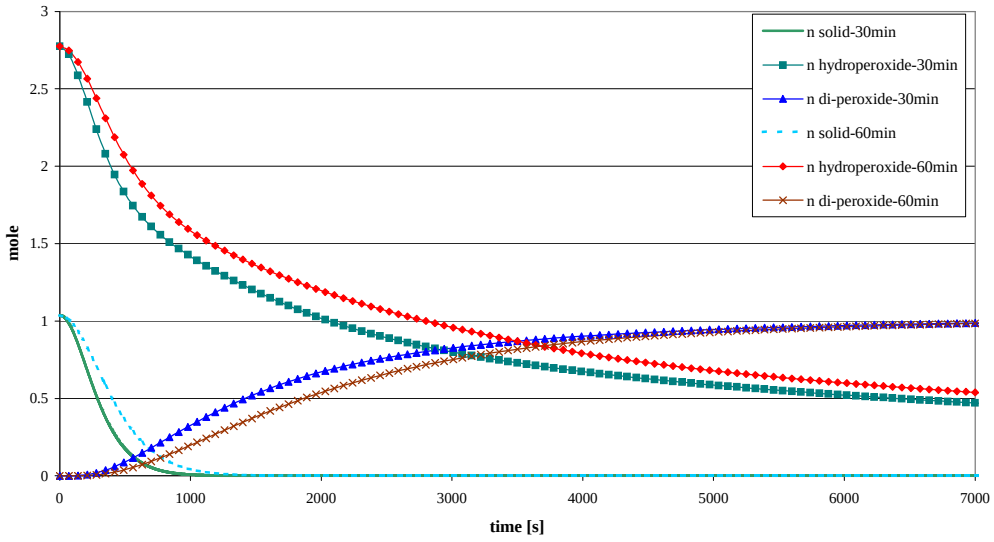


Figure 7.7: Production of di-peroxide at an addition of 30min and 60min

From the figure 7.5 above it can be seen that, following this simulation, the production of the di-peroxide has only slightly decreased, with the end of the addition after one hour, there is 0.8mole of di-peroxide produced, which is equivalent to a conversion of approximately 80%.

Another parameter that might enhance the safety of the process is the temperature. The results of the experiments in the RC1*e* at temperatures between 5°C and 20°C showed a stable process at 5°C while the experiment at 20°C ended up in a thermal runaway. To observe the influence of an even lower temperature, simulations at 5°C and 2°C were performed with the developed model and are presented in the following figure 7.8.

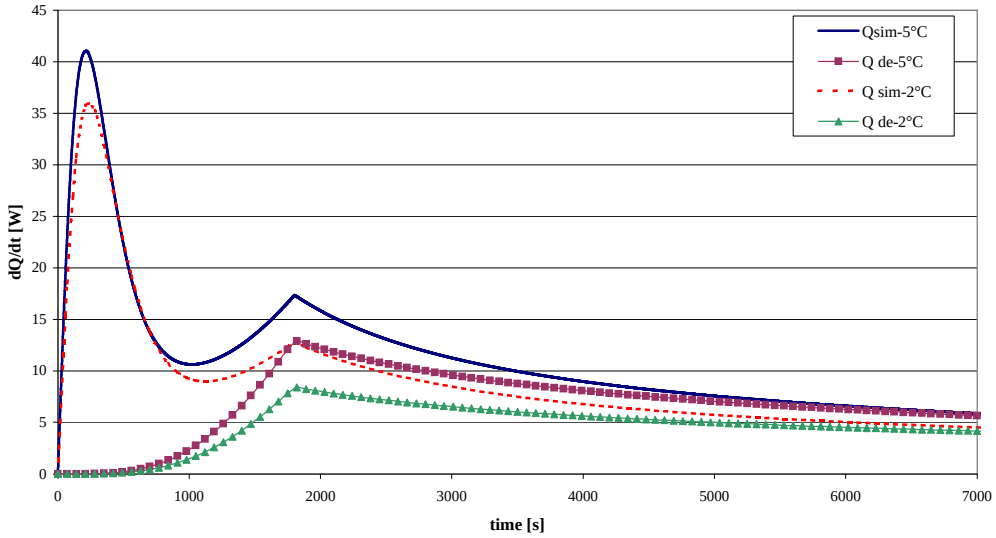


Figure 7.8: Comparison of heat production for temperatures at 2°C and 5°C

It can be observed from the figure 7.8 that the heat release rate is again lowered by this lower process temperature. To observe also the influence on the production of the di-peroxide, the increase of di-peroxide as well as the decrease of hydroperoxide and solid are shown in the next figure 7.9.

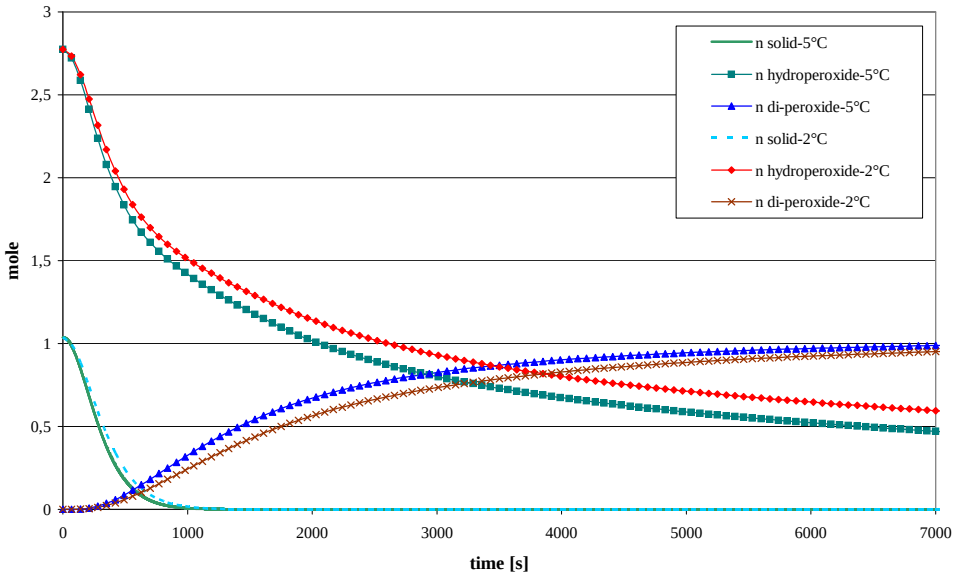


Figure 7.9: Production of di-peroxide for temperatures at 2°C and 5°C

This last figure shows that on the one hand the heat release rate is lowered by a process temperature of 2°C, but the production of the di-peroxide is also lowered. Now the conversion after one hour of the experiment is 72%.

Up to now, the recommendations for a safer process are only valid for the RC1*e*. For a scale-up, the different ratio of heat exchange area and volume (A/V) and the different mixing conditions always have to be considered. Following Steinbach [Steinbach 3] the change of this ratio of heat exchange area and volume (A/V) can be approximated with the following condition: $A/V^{2/3}$ = const. This means that with an increase in scale the heat exchange area decreases dramatically. Examples are also shown by Weber [Weber]: while a 1l reactor still has a cooling area of 500cm² ($A/V=50m^{-1}$), a pilot plant of 1m³ only has 5m² as cooling area ($A/V=5m^{-1}$).

As the exact conditions for a possible next scale (pilot plant) were unknown, no concrete calculations could be made concerning the scale-up of the process. A rough first estimation was made with the help of a simulation considering the changed ratio of heat exchange area and volume (A/V), but not the different mixing conditions. A simulated scale-up from the RC1*e*-scale to a 100l-scale showed that the process cannot be operated under the planned conditions. Even at a temperature of 5°C the addition time would have to be slowed down to several days to be able to control the released heat.

Even so it can finally be said that a scale-up to pilot scale should be possible, if a sufficient cooling capacity is guaranteed, the solid is of a small and consistent particle size (preferably <0.5mm), the system is diluted, the process temperature does not exceed 5°C and the addition of the catalyst is slowed down. As already discussed in chapter 7.2 a well diluted system would give an inherent safety margin at 100°C due to the evaporation of the water, always ensured that there is enough water to cool all released heat by evaporation and the cooling capacity of the condenser is sufficient. Before the performance of the experiment in pilot scale, all conditions have to be well calculated and simulated and a dilution is very much recommended.

Chapter 8:

Summary

In the presented work an organic peroxide synthesis was analysed. A di-peroxide was produced out of a hydroperoxide and a solid in a semi-batch reactor under the presence of a catalyst, which was gradually added. Because the first reaction partner was a solid, the second an organic liquid (hydroperoxide) and the catalyst an inorganic liquid, the reaction was a solid-liquid-liquid heterogeneous system. This newly developed, heterogeneous peroxide synthesis was highly reactive due to the great exothermal decomposition enthalpy of the peroxides and therefore not easy to handle concerning safety aspects.

Up to now, overall safety criteria for a complete and simple assessment of heterogeneous systems do not exist. The aim of the evaluation of this process was to give recommendations on a safe handling of it and further even for a safe scale-up of the process, from laboratory to pilot scale. For homogeneous reactions there is at least in Germany a good and often applied regulation for process safety called TRAS 410. As it would be good to expand the TRAS 410 to heterogeneous systems as well, the planned process was analysed and evaluated according to the scheme of the German technical regulation TRAS 410.

This regulation implies first checks of all involved substances in pure form. These checks showed that the solid itself does not carry any hazardous potential, but the two peroxides and their intermediate product do. Tests on the two peroxides and their intermediate showed that the hydroperoxide carries the highest risk potential, a maximum process temperature according to the 100K-rule was determined to 5°C. The tests furthermore showed that the decomposition of the hydroperoxide was catalysed by the catalyst as well as by the steel of the sample cells of the DSC. 5°C was then adopted as a maximum temperature for the pure substances, as all substances involved stayed stable at that temperature.

After the evaluation of the substances in pure form, the process was analysed under different aspects. Experiments in the mini-laboratory reactor showed that the addition time as well as the particle size of the solid have a great influence on the reaction. It was found that an addition of the catalyst batch-like ends up in a thermal runaway, while an addition time of at least 30min keeps the process relatively stable in the 250ml laboratory reactor and also at 1l-scale (reaction calorimeter RC1*e*). Concerning the analysis of the influence of the particle size it was evaluated that with increasing particle size of the solid the risk of a thermal runaway increases. As usually the reaction is decelerated with greater particles due to the lower relative surface, this result was unexpected. It is assumed that two phenomena are responsible for this behaviour. The first phenomenon could be explained with the help of pictures of the solids made by an electronic microscope. They show that the solid consists of agglomerated small particles. A „breaking-off“ of these particles caused by stirring offers a higher relative surface immediately and let the reaction rate increase and the temperature rise. Furthermore it is also well possible that with the smaller relative surface of the agglomerated particles, the catalyst was not completely used for the synthesis reaction and then the decomposition of the hydroperoxide is favoured instead of the synthesis, as the decomposition is also catalysed by the catalyst. It is assumed that the second phenomenon, the decomposition of the hydroperoxide, has the larger effect on the strong increase in temperature for the experiments with larger particles. Concluding these results, the addition time should be, depending on the scale, of at least 30min and the solid should be of small and consistent particles to ensure a safe handling of it and a safe scale-up.

The regulation TRAS 410 not only demands the evaluation of the process under normal conditions but also the analysis of possible process deviations. Therefore a so called worst case scenario is imagined, where the reactor is adiabatic, i.e. no heat is exchanged with the environment. This worst case scenario is then best to analyse in an adiabatic batch reactor. The process was therefore performed in the adiabatic batch ADC II from Chilworth. It showed a two-step mechanism, first the synthesis reaction and then the decomposition of the peroxides. The experiments showed that even at a start temperature of 3°C, the synthesis started immediately with the addition of the catalyst. The maximum pressure was higher than 25bar, as this was the maximum pressure tolerated by the apparatus. Further, evaluations of the experiments showed a first order kinetics for the decomposition of the perox-

ides. It was further figured out, that a dilution with water gives in an open system an inherent safety margin at 100°C, due to the evaporation, if there is a well operating condensing and reflux system. The adiabatic experiments clearly showed that a thermal runaway has to be avoided under all circumstances and that it would improve the safety of the system to operate it diluted with water.

Finally, isothermal experiments in the RC1*e* from Mettler Toledo were performed. This is especially helpful for a scale-up of a process, as the RC1*e* resembles the reactors of industrial scale. Experiments at 5, 10 and 15°C could be performed safely while an experiment at 20°C ended in a runaway. The analysis of these experiments showed that there is a parallel reaction system with the synthesis reaction on one side and the competing decomposition of the hydroperoxide on the other side. As the decomposition of the hydroperoxide is dependent on the temperature as well as on the concentration of the catalyst, the danger of a decomposition and a following runaway is highest with the end of the addition, because then the concentration of the catalyst has reached its maximum. A maximum process temperature of 5°C resulted from the experiments in the RC1*e*, at higher temperatures there was a too great decomposition of the hydroperoxide. The experiments further showed that the productivity of the process is not strongly decreased by lower process temperatures (5°C), that there is not even a need to keep to a process temperature of 15°C for economical reasons.

Kinetic parameters of the reaction synthesis are important to describe the process and to put up a model for the re-simulation of the measured data. With this verification of the measured data, simulations can be used to simulate different process conditions and predict the behaviour of the process, especially concerning the safety of the system. As the reaction system consisted of three reactions, two consecutive reactions, which form the synthesis reaction, and one parallel, the decomposition of the hydroperoxide, well approved methods to determine reaction kinetics for simple reactions could not be applied. Thus a model was put up to re-simulate the experiments in the RC1*e*. The first attempts for the simulation of this process showed that the consecutive reaction of the synthesis, first the production of an intermediate and then the formation of the di-peroxide, cannot be neglected. With this con-

secutive reaction and a simulated strong influence of the concentration of the catalyst on the decomposition, a final model was put up for the system. Then the experiments in the RC1*e* were successfully re-simulated.

Finally, a safety criterion for the isothermal semi-batch reactor developed by Steinbach [Steinbach 1] was applied and simulations were performed to give recommendations on a possible scale-up of the process from laboratory to pilot scale. With the help of the safety criterion, with a maximum temperature of 5°C a recommendation on a safe temperature range for the process could be given. The experiments in the RC1*e* as well as the application of the 100K-rule to the hydroperoxide and the simulations also showed that the process should be operated at a maximum temperature of 5°C. This was proven by the simulations, which further showed that a longer addition time would also improve the safety of the system. Experiments showed that the solid should be of a small, consistent particle size to avoid a favouring of the decomposition reaction of the hydroperoxide and a sudden rise in process temperature. The addition time of the catalyst should be of at least 30min for the RC1*e* at 1l-scale. A further increase in safety is achieved if the process is diluted with water, if a good condenser and reflux system is guaranteed.

First simulations for an estimation of the behaviour of the process at 100l-scale showed that with the decreasing ratio of cooling area to volume (approximately 1:44 for the 1l-scale, but 1:5.3 for the 100l-scale) the process cannot be operated as planned as the cooling system will possibly not be able to control the released heat. But for a diluted system under the presented conditions a safe scale-up from laboratory to pilot scale should be possible.

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Appendix

A.1 Results from the DSC

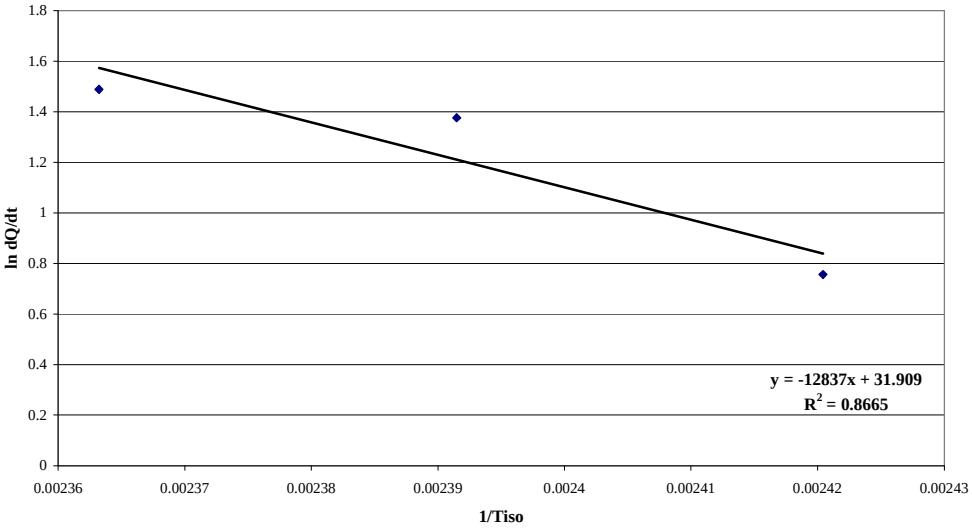

Figure A.1: Determination of E/R for the hydroperoxide

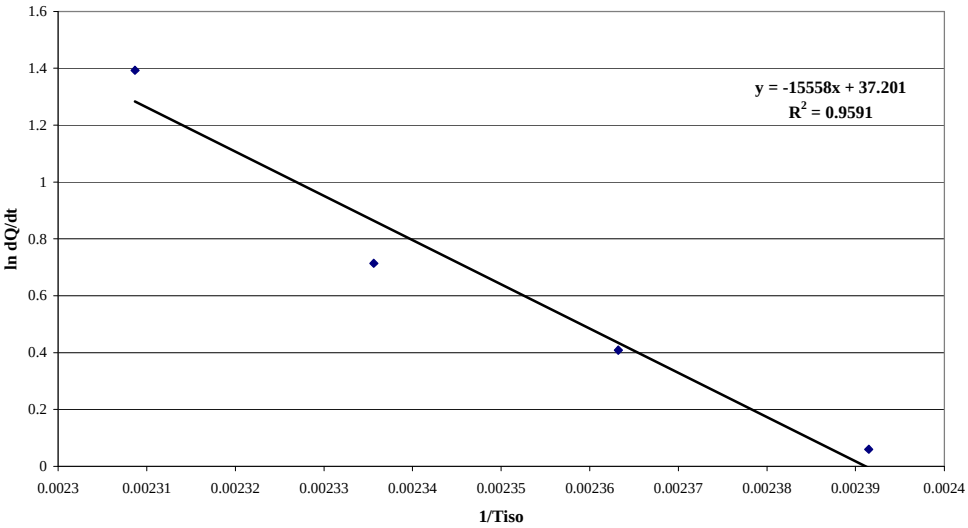

Figure A.2: Determination of E/R for the intermediate

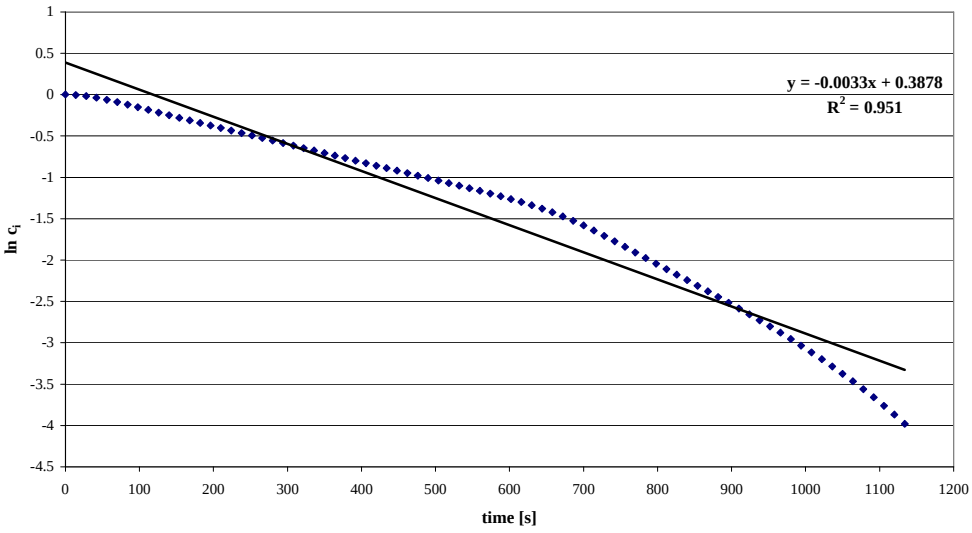

Figure A.3: Prove for first order kinetics for the intermediate at 145°C

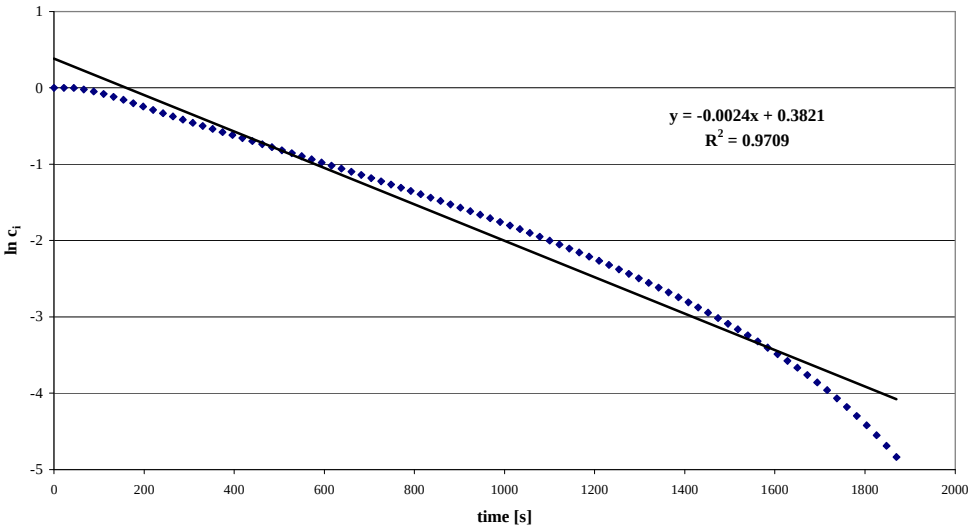

Figure A.4: Prove for first order kinetics for the di-peroxide at 150°C

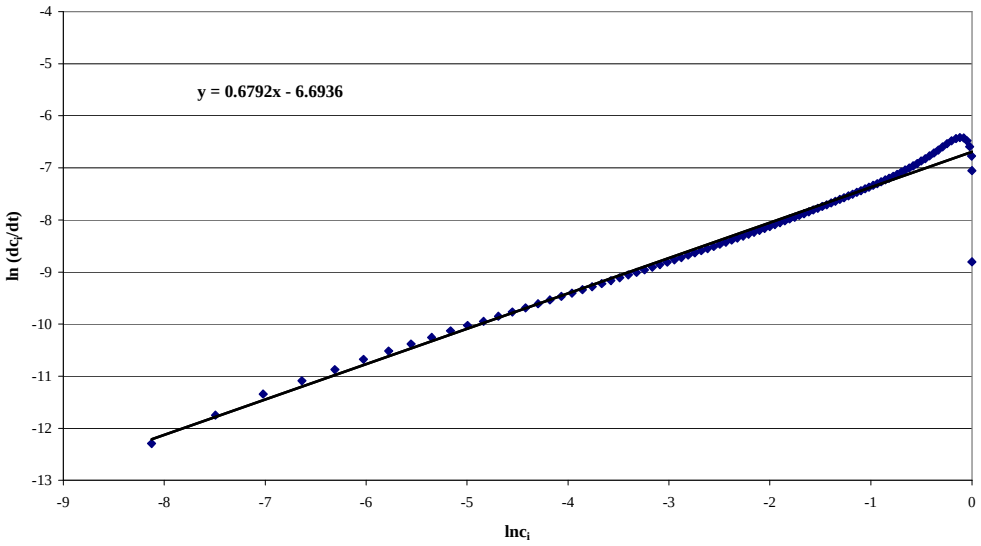

Figure A.5: Determination of reaction kinetics for the di-peroxide by differentiation

A.2 Results from the TEVT

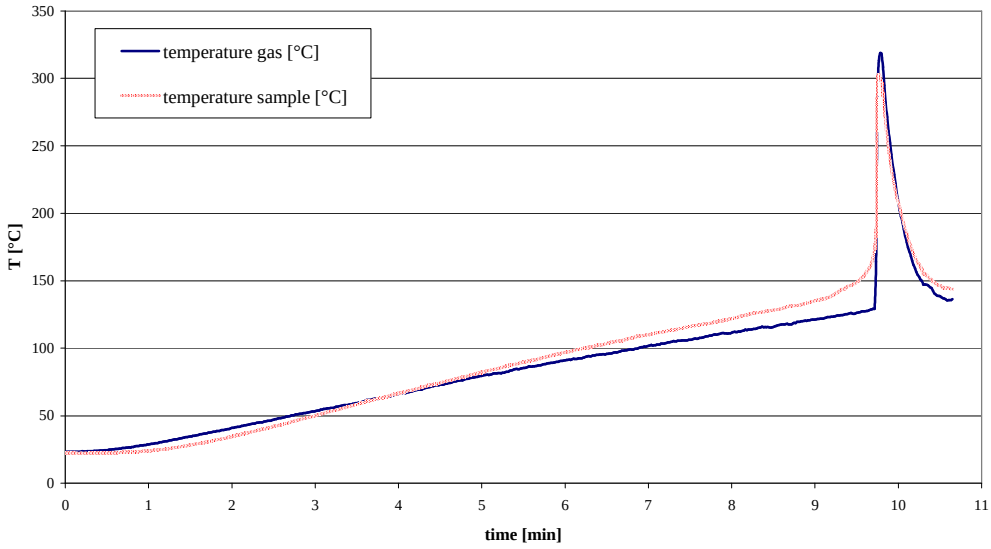

Figure A.6: Temperature curve from 5g di-peroxide in the TEVT, max p 20.7bar

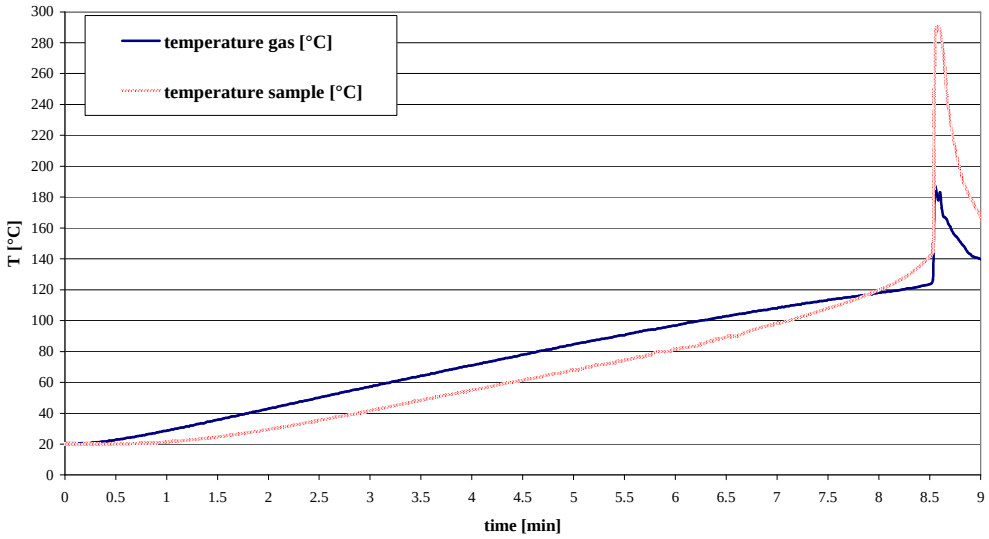

Figure A.7: Temperature curve from 5g intermediate in the TEVT, max p 25.1bar

A.3 Simulation programs

A.3.1 Simulation program for the adiabatic batch reactor

```
; file  ***************** ADIABATIC_BATCH.MMD  *****************

METHOD auto
STARTTIME = 0
STOPTIME=1000
DTOUT=1
; ******************   Definition of the parameters    -Simulations************

koo=1.2*10^6          ; pre-exponential factor in l/mol s
VBR=0.19                    ;volume in l
ER=6250                ; activation temperature in K
cA0=1.6                  ; concentration in mole/l
DRH=220000             ; enthalpy in J/mole
phi=1.4                     ; phi-faktor
rhoCp=1700             ; product of density and heat capacity in J/(K·l)

TCelsius=323             ; starting temperature in K
;+++++++++++++++++++++++++++++++++     equations  ++++++++++++++++++++

d/dt(XA) = koo*exp(-ER/T)*(1-XA)        ; mass balance
init(XA)=0                                      ; starting value for conversion
d/dt(T)=DRH*koo*exp(-ER/T)*cA0*(1-XA)/(rhoCp*phi)      ; heat balance in W
init(T)=TCelsius
```

A.3.2 Simulation program for the isothermal semi-batch reactor (RC1*e*)

```
; file ***************     ISOTHERMAL_SEMIBATCH.MMD   ******************
METHOD auto
STARTTIME = 0
STOPTIME=7200
DTOUT=1
; ******************        Definition of the parameters    -Simulations  ***************
nueA=-1     ; stoichiometric coefficient of the added component (catalyst)
nueB=-1     ; stoichiometric coefficient of the first component in the reactor (solid)
nueC=-1    ; stoichiometric coefficient of the first component in the reactor (hydroperoxide)
nad=3.7                    ; added amount of catalyst
nB0=0.28*nad               ; amount of solid in the reactor at start
nC0=0.75*nad               ; amount of hydroperoxide in the reactor at start
nIM0=0                     ; amount of intermediate at the start
taudos=1800            ; addition time in s
koo3=5.32*10^9         ; pre-exponential factor (l/mole·s) for the reaction to the di-peroxide
koo2=1.86*10^6         ; pre-exponential factor (l/mole·s) for the reaction to the intermediate
koo1=2.8743*10^14 ; pre-exponential factor (l^4.6/mole^4.6·s), decomposition hydroperoxide
ER3=8704               ; activation temperature in K, reaction to the di-peroxide
ER2=5840               ; activation temperature in K, reaction to the intermediate
ER1=13717              ; activation temperature in K, decomposition of the hydroperoxide
p=4.6                  ; exponential factor for the catalyst
m=1                    ; exponential factor for the hydroperoxide
VBR=0.91               ; volume with the end of addition in l
epsilon=0.5            ;   volume increase factor
kw=160                 ;overall heat transfer coefficient in W/K·m²
F=0.04                 ; heat transfer area in m²
DRH3=16000             ; enthalpy in J/mole reaction to di-peroxide
DRH2=16000             ;  enthalpy in J/mole reaction to intermediate
DRH1=172800            ; enthalpy in J/mole decomposition of the hydroperoxide
```

```
rhoCp=2000              ; product of density and heat capacity in J/(K·l)
Tiso=Tdos               ; addition temperature in K (!)
TCelsius=5          ; isothermal reaction temperature in K (was changed)
Tdos=(273.15+TCelsius)
;+++++++++++++++++++++++++++++++++  equations  ++++++++++++++++++++
T=TCelsius
d/dt(nB) = -k2*nA*nB*nC/(Vol^2)       ; mass balance for the solid
d/dt(nC) = -k1*(nC/vol)^m*(nA/vol)^p*(Vol)-k2*nA*nB*nC/(Vol^2)- k3*nC*nA*nIM/
(Vol^2)                 ; mass balance for the hydroperoxide
d/dt(nIM)=k2*nA*nB*nC/(Vol^2)-k3*nC*nA*nIM/(Vol^2)   ; mass balance intermediate
init(nC)=nC0                                        ; start value for the hydroperoxide
init(nB)=nB0                                          ; start value for the solid
init(nIM)=nIM0                                      ; start value for the intermediate
nA=nad*(theta)                                  ; amount of catalyst in mole at moment t
theta=time/taudos                                     ; dimensionless time
LIMIT theta<=1                                       ; maximum of theta is 1
Qpunkt=Qpunkt1+Qpunkt2+Qpunkt3  ; released heat [W]
Qpunkt1=DRH1*(k1*(nC/vol)^m*(nA/vol)^p*(Vol)); released heat [W] decomposition
Qpunkt2=DRH2*k2*nB*nA*nC/(Vol^2)  ; released heat [W] production of intermediate
Qpunkt3=DRH3*k3*nIM*nA*nC/(Vol^2)   ; released heat [W] production of di-peroxide
next SUMQ=SUMQ+Qpunkt               ; summed heat
init SUMQ=0                          ;initial value summed heat
init n=0                    ; initial value for counting number of heat
next n = n+1
nL180=nB0-nB-nIM          ; actual amount of di-peroxide
Xtherm=SUMQ/81834         ; simulated thermal conversion
k2=koo2*exp(-ER2/Tiso)    ; reaction rate constant for the reaction to the intermediate
k3=exp(-ER3/Tiso)*koo3    ; reaction rate constant for the reaction to the di-peroxide
k1=koo1*exp(-ER1/Tiso)  ; reaction rate constant decomposition of the hydroperoxide
Tw=Tiso+epsilon/(1+epsilon)*(Tiso-Tdos)/(taudos/taucool)-Qpunkt/(VBR*rhoCp/tau-
cool)  ; cooling temperature in K
DeltaT=(Tiso-Tw)                ; temperature difference (Tinside reactor - Tjacket) in K
```

Tkmin=Tiso-DeltaTad/((epsilon/(1+epsilon))+(taudos/taucool)) ; minimum cooling temperature in K

Vol=(1+epsilon*theta)*VBR /(1+epsilon) ; volume as a funtion of time in l

taucool=(VBR*rhoCp)/kw*F ; time constant of cooling in 1/s

DeltaTad=(DRHS)/(rhoCp*VBR) ; adiabatic rise in temperature in K

DRHS=DRH1*Xie1+DRH2*Xie2+DRH3*Xie3 ; total reaction enthalpy

Xie2=(nB0-nB)/(nC0+nB0) ; extent of reaction for the production of the intermediate

Xie3=(nIM)/(nC0+nB0)+Xie2; extent of reaction for the production of the di-peroxide

Xie1=(nC0-nC)/(nC0+nB0)-Xie2-Xie3; extent of reaction, decompositon of hydroperoxide

A.4 Simulations of the experiments in the RC1*e*

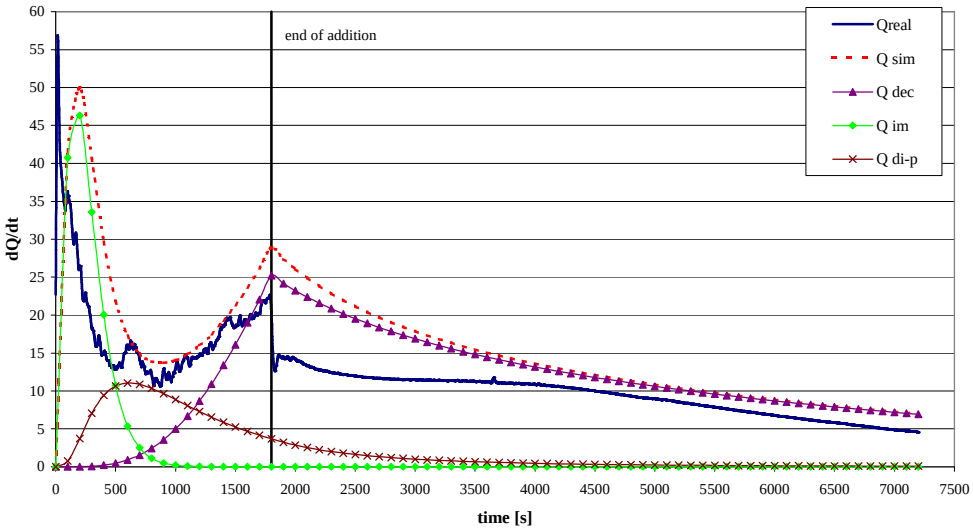

Figure A.8: Simulation of the experiment at 10°C, heat release rate

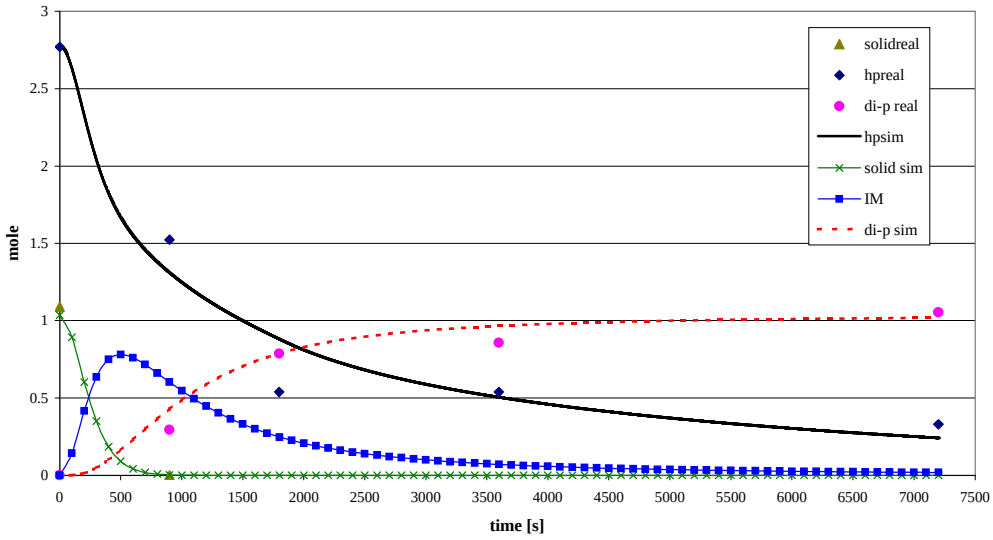

Figure A.9: Simulation of the experiment at 10°C, mass balances

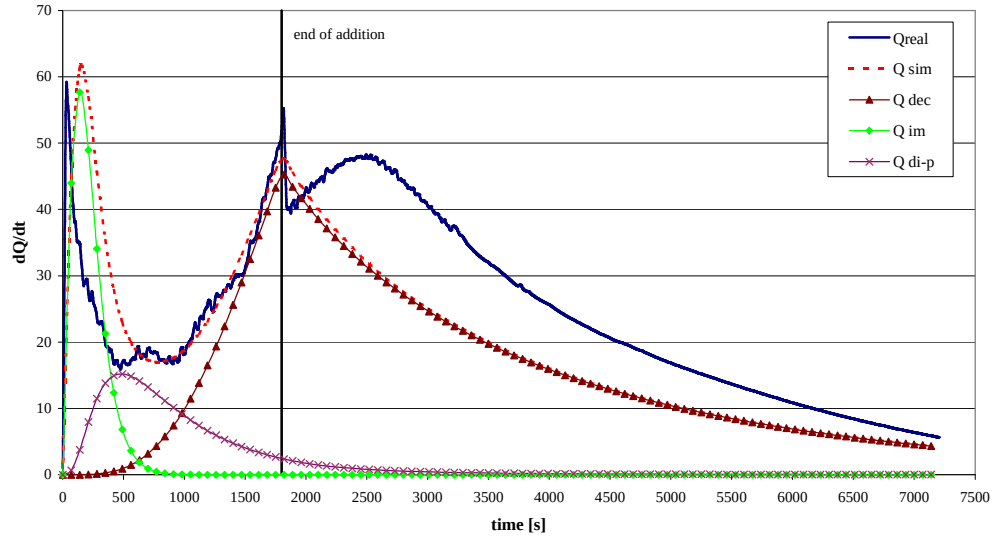

Figure A.10: Simulation of the experiment at 15°C, heat release rate

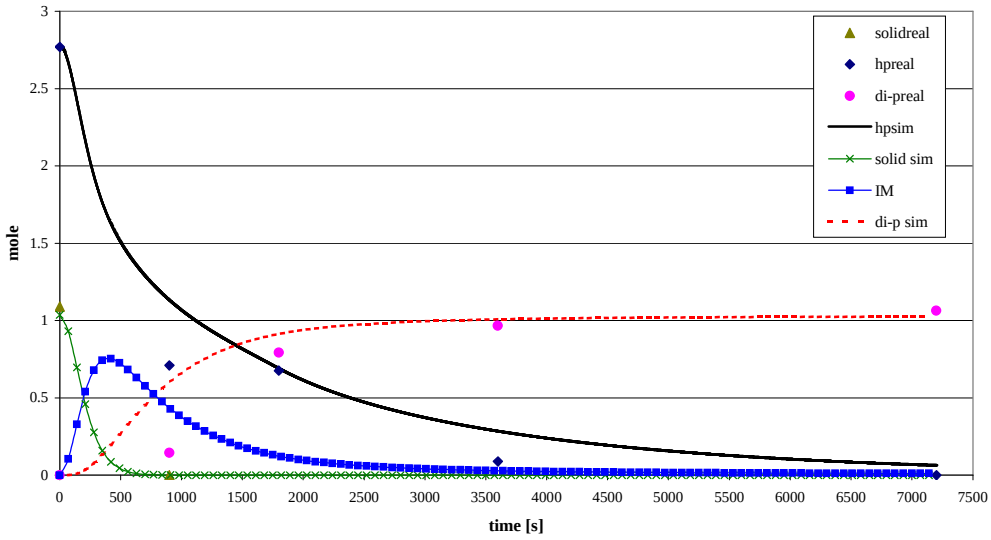

Figure A.11: Simulation of the experiment at 15°C, mass balances

A.5 HPLC-program

Apparatus:

Apparatus Agilent 1100 equipped with

- Autosampler
- Quartenary pump
- Diode array detector

HPLC column MODULO-CART EXPERT „INTERCHIM“, 25cm x 4.6mm i.d., dp = 5µm

Solvents:

- Acetonitrile from Roth, HPLC grade
- Water from Roth, HPLC grade
- Methanol from Roth, HPLC grade

Standard preparation:

Approximately 2g of hydroperoxide are accurately weighed into a 100ml volumetric flask, diluted to volume with acetonitrile and inverted several times to mix the solution.

Approximately 1g of solid are accurately weighed into a 100ml volumetric flask, diluted to volume with methanol and inverted several times to mix the solution. 1ml of this solution is transfered into a 10ml volumetric flask and diluted with acetonitril and inverted several times to mix the solution.

Sample preparation:

Approximately 0.1g of the product are accurately weighed into a 100ml volumetric flask, diluted to volume with acetonitrile and inverted several times to mix the solution.

Instrumental parameters:

Flow: 1ml/min
Detection: UV at 200nm
Injection volume: 10µl
Mobile phase. gradient program as follows

time [min]	water [%]	acetonitrile [%]	gradient
0	85	15	-
1	85	15	linear
5	65	35	linear
10	40	60	linear
35	5	95	linear
40	0	100	linear
50	0	100	linear
55.1	85	15	linear

The solid is then found after a retention time of 9.89min (para) and 10.07min (meta), the hydroperoxide after a retention time of 11.14min, the intermediate after 26.08min (meta) and 26.50min (para) and the di-peroxide is finally found after 45.31min (meta) and 45.75min (para).