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Master Thesis

# Analysing the hydration reaction of boron oxide in selected solvents

performed for the purpose of obtaining the academic degree of master of science  
under the supervision of

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# Affidavit

I, Katharina Wagner, hereby declare

1. that I am the sole author of the present Master Thesis, "Analysing the hydration reaction of boron oxide in selected solvents", 101 pages, bound, and that I have not used any sources or tool other than those referenced or any other illicit aid or tool.
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\_\_\_\_\_  
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# Kurzfassung

Eine vielversprechende Technologie zum Speichern von Wärme sind thermochemische Energiespeicher. Hierbei wird Wärme als Reaktionsenthalpie gespeichert und kann über die Rückreaktion wieder freigegeben werden. Über diese Technologie ist es möglich anfallende Abwärme zu speichern und somit die Effizienz einer Anlage zu steigern. Zusätzlich wird durch den Einsatz von Speichern die Installation von erneuerbaren Energiequellen erleichtert, da die schwankende Produktion dieser ausgeglichen werden kann.

Eines dieser Speichersysteme ist das System  $B_2O_3/H_3BO_3$ . Für diese Arbeit wird die Wärmefreisetzung studiert. Diese folgt der Reaktion



Bei einer Vorarbeit wurde festgestellt, dass ein hoher Wasserüberschuss nötig ist, um das entstehende Gemisch homogen mischen zu können. Aufgrund des hohen  $c_p$ -Wertes von Wasser, senkt das die maximal erreichbare Temperatur. Deshalb wurde untersucht, einen Teil dieses Wassers durch ein Suspensionsmittel mit einem niedrigeren  $c_p$  zu ersetzen und somit die resultierende Temperatur zu steigern.

Während der Versuche wurde ebenfalls die Reaktion zwischen Alkoholen und Bortrioxid auf ihre Eignung als thermochemischer Energiespeicher untersucht.

Nach der Untersuchung mit mehreren Lösungsmitteln wurde eine detaillierte Studie in ausgewählten Lösungsmittel durchgeführt. Hierbei wurden verschiedene Starttemperaturen und verschiedene Massenverhältnisse zwischen den reagierenden Stoffen zu dem Lösungsmittel durchgeführt. Zusätzlich wurde ein Vergleich zu der Reaktion ohne Lösungsmittel angestellt. Ein weiterer Vergleich wurde zwischen einer Suspension in Lösungsmittel und einer Reaktion in reinem Wasser angestellt. Hierbei wurde der maximale Temperaturhub betrachtet.

Die Ausbeute wurde ermittelt über verschiedenste Analysemethoden, als auch über eine Berechnung über die Temperaturerhöhung.





# Abstract

Thermochemical energy storage is a promising technology to store heat. The heat is stored as reaction enthalpy and can then be released again via the reverse reaction. With this technology it is possible to store waste heat and therefore increase the efficiency of a plant. Additionally, it is easier to install renewable energy sources since it is possible to counter the fluctuating energy production of these kind of plants.

One of these storage systems is the system  $B_2O_3/H_3BO_3$ . In this thesis the heat production is studied. This follows the reaction



A preceding work showed, that a high water excess is necessary to ensure homogeneous mixing of water and boron oxide. But since water has a relatively high  $c_p$ -value, this excess water reduces the maximal reachable temperature. To counter this, some of the water was substituted with a solvent with a lower  $c_p$ , therefore increasing the maximal temperature.

During the experiments, also the reaction between alcohols and boron trioxide was tested for their possibility as thermochemical energy storage.

After a broad study of various solvents, a more detailed study with selected solvents followed. Therefore, various starting temperatures as well as various mass relationships between reacting agents and solvent were tested. Additionally, a comparison with the reaction without solvent was done.

An additional comparison was done between a suspension in solvent and a suspension in pure water. The observation criterium was the temperature increase during the reaction. This was higher in methyl isobutyl ketone, compared to pure water.

The conversion was determined by various analytical methods, as well as with a calculation using the temperature increase over the reaction time.



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# Chapter 1

## Introduction

### 1.1 Energy consumption

The energy demand of the modern civilization nearly doubled in the time between 1980 and 2012 [1], visible in figure 1.2. This development is part of a long-lasting increase of humanities energy demand, starting from the time our predecessors used fire to cook meat and heat with it, as seen in figure 1.1 [2].

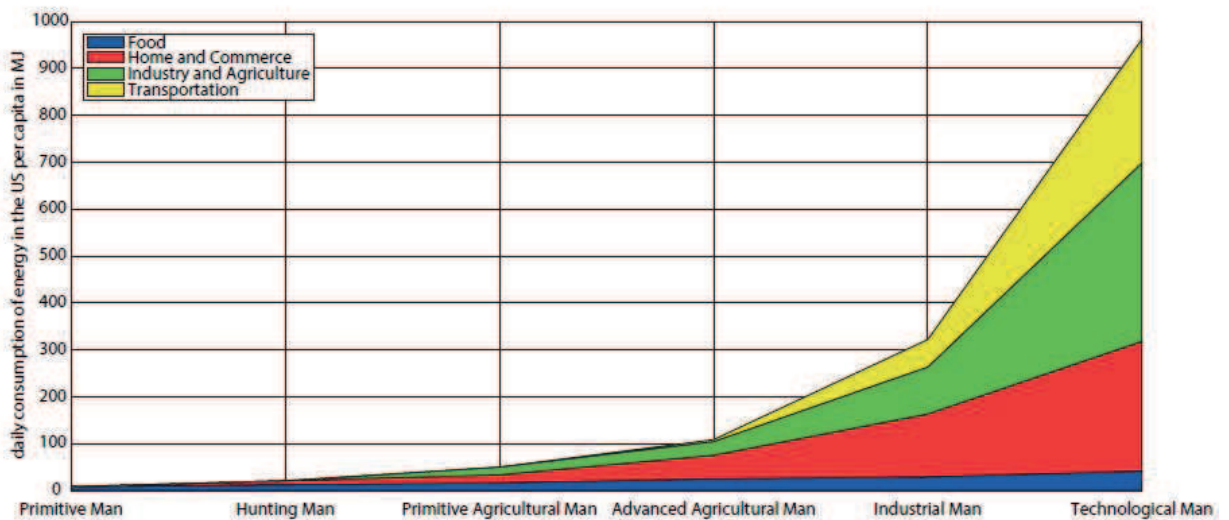


Figure 1.1: Estimated daily consumption of energy per capita in the U.S. for different eras adapted from [2].

The ever increasing demand of energy in our society not only asks for more energy production but also corresponds with various difficulties. Since most of the energy is still produced by non-renewable resources, CO<sub>2</sub> emissions and the limited amount of those just count for some of these negative effects. When trying to reduce non-renewable resources and replacing them with renewable sources like wind power or solar energy other problems occur. The nature of these power production plants is that they mainly produce energy while the demand is low and are not able to produce energy during times with high demand [3, 4].

To still be able to use renewable energy sources instead of oil and natural gas it is necessary to be able to store energy over certain time periods. This way, the fluctuating energy production of renewable energy does not pose a problem. Following this route it would be possible to

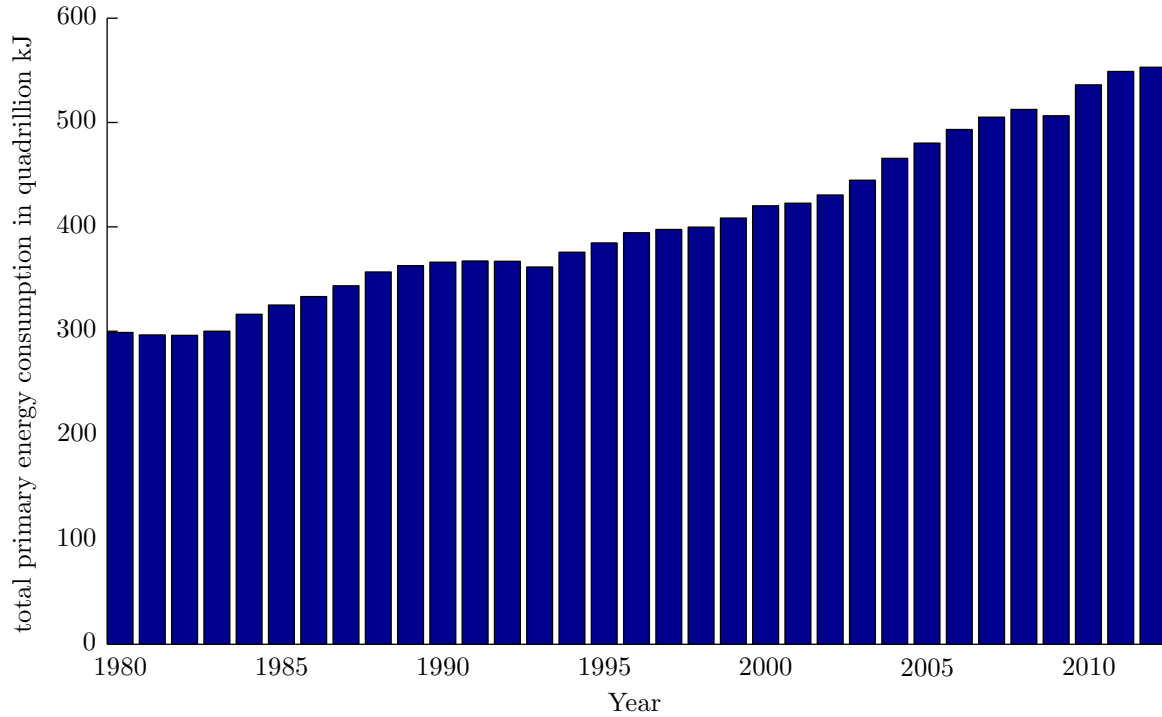


Figure 1.2: Worldwide primary energy consumption per year [1].

supply energy while the demand is high and store energy while the demand is low [4, 5, 6].

## 1.2 Energy storage systems

Energy storage systems store energy produced at one time for use at a later time. Depending on the type of energy the medium stores, different storage systems are applicable. Table 1.1 gives an overview of the different energy types and the used storage systems for each one of them.

Table 1.1: Energy storage (ES) systems sorted by the stored energy type [6].

Mechanical ES	Chemical ES	biological ES	magnetic ES	thermal ES
<ul style="list-style-type: none"> <li>• Hydrostorage</li> <li>• Compressed air storage</li> <li>• Flywheels</li> </ul>	<ul style="list-style-type: none"> <li>• Electrochemical batteries</li> <li>• Organic molecular storage</li> </ul>			<ul style="list-style-type: none"> <li>• sensible heat storage</li> <li>• latent heat storage</li> <li>• Chemical heat storage</li> </ul>

### 1.2.1 Mechanical energy storage

One of the several mechanical energy storage systems is the compressed air energy storage (CAES). This method uses excess electricity instead of gas to compress air. The compressed

air is stored either in a rock cavern, salt cavern, depleted gas fields or an aquifer. While discharging the storage, the gas is first preheated and then entering a turbine to produce electricity. Since the air has to be preheated it is still necessary to use some natural gas but it is possible to produce three times more electricity than with a normal gas turbine. Other advantages of this technology are a fast reaction time and cycle stability [7].

A new technology called advance adiabatic CAES (AA-CAES) gets rid of the before needed gas. Here a thermal energy storage (TES) is used to store heat due to compressing of air and storing it to reheat the air for expansion. This heat is used to heat up the air before discharging and expanding it [8].

Another way of storing energy mechanically are flywheel energy storages (FES). For this system a rotor is spinning storing inertial energy. FES can be divided in low speed and high speed FES, where low speed FES deliver high power capacities in a short time and high speed FES do exactly the opposite [9].

The most energy can be stored with a pumped hydro energy storage (PHES) where water is pumped uphill when excess electricity is available. When too little electricity is produced, the water is released again powering a generator [10].

### 1.2.2 Electrical energy storage

The most commonly known electrical energy storage are batteries. Batteries release electricity by a chemical reaction. Depending on the used reaction different voltages, storage capacities, cycle stability and other parameters can be adjusted. Examples for batteries are lead-acid, nickel batteries and lithium batteries [11].

Another type of electrical energy storage are flow batteries. These have two containers filled with components dissolved in a liquid which are separated by a membrane [12].

Apart from batteries, another storage for electrical energy are superconducting magnetic energy storages, where energy is stored in a magnetic field. This is possible by cooling the material below its superconducting critical temperature [13].

### 1.2.3 Chemical energy storage

One of the most commonly mentioned chemical energy storages is hydrogen. If it is produced from renewable resources it has no greenhouse emissions and therefore contributes to the reduction of greenhouse gases [14].

### 1.2.4 Thermal energy storage

Thermal energy storage is one of the most versatile storage systems. It can be used for heating and cooling but also for high temperature applications. Furthermore it is possible to increase the efficiency of a plant. In general thermal energy is stored by changing the internal energy of the material [15].

In a sensible heat storage (SHS) system the material changes its temperature depending on the amount of heat added, the heat capacity of the material and the amount of material. This system either uses liquids, here mainly water and sometimes oil, or solid materials like rock or sand. An important factor is that the phase of the material does not change when storing energy. Water is one of the most used storage mediums for sensible energy storage since it is widely available, non-toxic and non-combustible, has high specific heat

and a rather high density. Unfortunately water is limited by its freezing and boiling point and therefore only usable for applications inside these boundaries [16].

Latent heat storage (LHS) describes an energy storage medium that undergoes a phase change during charging and discharging. The energy is stored as latent heat of the phase change. One major advantage of LHS over SHS is the high energy density compared to nearly zero temperature elevation. Drawbacks are often a low heat conductivity, phase segregation and restricted cycle stability [16].

Another thermal energy storage are thermochemical energy storages. These are further described in the next section.

### 1.2.5 Thermochemical energy storage

Here energy is stored by undergoing an endothermic reaction. Normally this reaction is a decomposition reaction so the reaction products can be stored separately. As long as the reactants are stored adequately and no unwanted reactions occur, the storage does not have any losses. The main loss entails cooling after charging and heating before discharging. For discharging the separated products are brought together and react back in an exothermic reaction to release the stored heat [17]. This procedure can be seen in figure 1.3 and follows reaction 1.1.

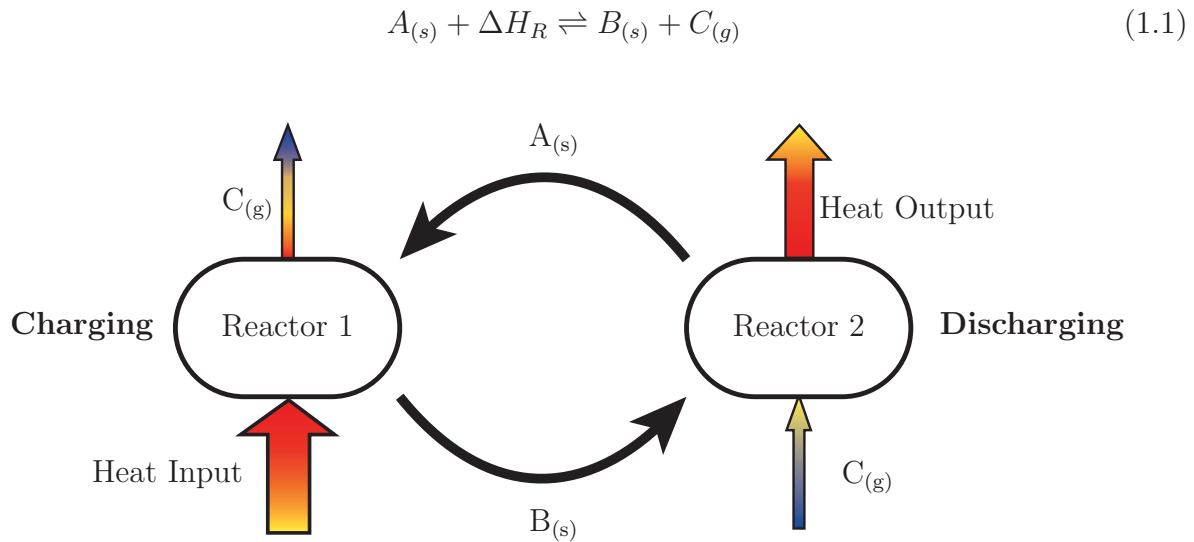


Figure 1.3: Reaction loop of thermochemical energy storages. The heat input into Reactor 1 decomposes A into B and C. In Reactor 2 B and C react back to A, producing heat in the process [18].

Like already mentioned, one of the advantages of this system is the minor heat loss during storing. Another advantage is the higher energy density compared to LHS and SHS. This storage is suited to be used for long term storage, also including several months.

Parameters that have to be accounted for when choosing a thermochemical storage material are cycle stability, energy storage density, reaction rate, the usable temperature range, heat transfer, cost, toxicity, flammability and corrosiveness. According to these criteria table 1.2 shows promising materials investigated by Visscher et al [19].

The system studied throughout this work is  $B_2O_3/H_3BO_3$ . This system has an energy storage density of  $864.86 \frac{kJ}{kgB_2O_3}$  at standard conditions and is a low temperature storage, producing

Table 1.2: promising thermochemical storage materials

Material	Formula	solid reactant + fluid	energy storage density (GJ/m <sup>3</sup> )	charging temp. °C
magnesium sulfate	MgSO <sub>4</sub> · 7H <sub>2</sub> O	MgSO <sub>4</sub> + H <sub>2</sub> O	2.8	122
iron carbonate	FeCO <sub>3</sub>	FeO + CO <sub>2</sub>	2.6	180
iron hydroxide	Fe(OH) <sub>2</sub>	FeO + H <sub>2</sub> O	2.2	150

temperatures in the range of 50-100 °C [20]. The discharging reaction can be seen in equation 1.2.



### 1.3 Aim

The aim of this thesis is to further study the system B<sub>2</sub>O<sub>3</sub>/H<sub>3</sub>BO<sub>3</sub> regarding its potential as a thermochemical energy storage. This system is characterized by the fast discharging reaction and is further studied as continuation of the work by Karel et al. [21], which focused on the reaction with gaseous water. In this work the system is studied with liquid water as one reactant. The excess water needed to guarantee homogeneous mixing lead to a low reaction temperature due to the high  $c_p$  of water [20]. To increase the reaction temperature, some of the water was substituted by different solvents to increase the maximal temperature and study the effects different solvent classes have on the reaction.





# Chapter 2

## Fundamentals

This chapter gives a short overview of the terms and definitions used throughout this work. Later on, the materials used throughout this thesis are shortly characterized, as well as the analytical methods used for this work.

### 2.1 Theoretical basics

#### 2.1.1 Solution

If two substances are mixed homogeneously a solution occurs. The material dissolving the other is called the solvent and the dissolved substance is the solute. Most of the times the solvent is a liquid and the solute can be a solid, another liquid or gas [22].

#### Polarity of a liquid

Solvents are normally categorized into polar and non-polar solvents. One value to measure the polarity is the dielectric constant. Normally a solvent with a dielectric constant below 15 is considered non-polar [23]. The constant compares the reduction of the strength of the electric field surrounding a charged particle in a solvent with the field strength around this particle in a vacuum [23]. Depending on their differences in polarity two solvents are miscible, partly miscible or non-miscible.

Examples for dielectric constants are summarized in table 2.1. The values in this table correlate with the miscibility described later in 2.2.6.

Polar solvents can be further divided into protic and aprotic solvents. These characteristic might have the biggest influence on interactions between solvent and solute. If the molecular structure of a solvent includes a O-H or a N-H bond these solvents are hydrogen donors or

Table 2.1: Dielectric constant for various liquids [24].

solvent	dielectric constant
heptane	1.92
ethyl acetate	6.02
methyl isobutyl ketone	13.11
acetone	20.7
methanol	32.7
water	80.1

protic solvents. If the hydrogen is only attached to carbon atoms it is normally not acidic enough to form hydrogen bonds. These solvents are classified as aprotic [23].

### 2.1.2 Colloid

In a colloid, one substance is dispersed inside a second substance [25]. They are the intermediate between solutions and suspensions [26]. If light is shined through a colloid the particles inside scatter the light. This so-called Tyndall-effect separates a colloid from a solution which does not scatter light [27].

### 2.1.3 Suspension

In a suspension particles of one substance are distributed in another substance. Compared to a colloid the particles are bigger; they can be seen in a microscope or with the naked eye. In contrast to particles in a colloid, particles inside a suspension precipitate if the suspension is standing still [28].

### 2.1.4 Reactions in solvents

Solvents influence the changing configurations of reacting species, compared to reactions in the gas phase, where the configurations are not influenced by the surrounding medium. Furthermore, interactions between solvent and reactant and solvent-solvent interactions have to be taken into account, when a reaction is observed in a solvent.

One way, that a solvent can influence a reaction is by affecting the electrostatic interactions between charges. The solvent reduces the field strength of the reactants' charges and the forces acting on the charges. These phenomena are quantified by the relative permittivity  $\epsilon_r$  and the larger the value of  $\epsilon_r$ , the smaller the interaction forces between the charges.

The second parameter is the viscosity of a solvent. The higher the viscosity  $\nu$  the more the molecules are hindered in their movements.

Lastly, the polarizability  $\alpha$ , which measures to what extent it is possible to distort the electronic distribution over a molecule by the electric field of charged particles, or dipolar molecules [29].

Following these parameters a solvent can influence the reaction mechanism, the magnitude of the rate constant and the reacting species. It can also affect the ion pairing, complexing, hydrogen bonding and other association phenomena.

Reactions of ions and polar molecules occur readily in solutions. On the other hand, reactions involving molecular and free radical species, the typical reactions in the gas phase, occur less frequent in solution. In solution many intermediates are present in equilibrium concentrations; in the gas phase they are normally found in steady state concentrations. Additionally, the steady state concentrations cannot be studied independently of the reaction but it is possible to study equilibrium concentrations easily. The kinetic analysis might therefore be easier in solution than in the gas phase.

The activated complex is normally of molecular-type structures in gas phase reaction, but in solution they are mostly charged or charged-separated structures. The permittivity of the solvent influences the structure of the activated complexes and their charge distribution. Also the shape and size of the activated complex is mainly decided by the solvent. On the other hand also the structure of the solvent might be altered while forming an activated complex.

Before a reaction can occur, the reactants have to diffuse together. In the gas phase this occurs rather fast and therefore has no influence on the reaction rate. In a solution on the other hand, the diffusion might be the rate determining step. Also the movement of molecules is influenced in solvents by Brownian motion giving the molecules irregular paths. This influences some reactions.

Due to the difficulty to calculate partition functions in solution, the reaction calculations are based on thermodynamic formulations of the transition state theory [29].

### 2.1.5 Reaction heat enthalpy

An important part of a thermochemical energy storage system is the heat that can be stored inside the system. This reaction energy can be calculated by summing up the heat of formation of all participating substances.

$$\Delta H_R(T) = \sum \nu_i \Delta H_i(T) \quad (2.1)$$

$\Delta H_R$  ... reaction heat

$\nu_i$  ... stoichiometric factor for compound i

$\Delta H_i$  ... heat of formation of compound i

The stoichiometric factors are positive if the substance is a product and negative if the substance is a reactant.

The enthalpy of a compound needed in equation 2.1 is calculated by equation 2.2.

$$\Delta H_i(T) = H_i^0 + \int_{T_0}^{T_p} c_{p,i} dT' + \Delta H_i^p + \int_{T_p}^T c_{p,i} dT' \quad (2.2)$$

$H_i^0$  ... standard heat of formation for compound i at 25 °C and 1 atm.

$c_{p,i}$  ... heat capacity of compound i

$\Delta H_i^z$  ... heat of phase change for compound i

$T_p$  ... phase change temperature

$T_0$  ... 25 °C, reference point for standard heat of formation

$T$  ... upper temperature limit, the temperature for which the enthalpy of formation is calculated.

The last two terms of the equation describe a phase change of the substance. If no phase change occurs, this part can be neglected and it is possible to integrate from  $T_0$  to  $T$  in one step. For this work only the temperature range of 0 °C to 100 °C is studied. Since none of the participating substances changes its phase in this range, the last two terms can be neglected.

The heat capacity  $c_p$  describes the amount of energy that is needed to heat the material for 1 °C. It can be approximated by parameters in the following way [30]

$$c_{p,i}(T) = A + 10^{-3}BT + \frac{10^5 C}{T^2} + 10^{-6}DT^2 \quad (2.3)$$

$A, B, C, D$  ... heat capacity coefficients

$T$  ... temperature in Kelvin

Since the integrated form of  $c_p$  is needed in equation 2.2 the integrated form of formula 2.3 is given by equation 2.4.

$$\int_{T_0}^T c_{p,i} dT = \left( AT + \frac{10^{-3}BT^2}{2} - \frac{10^5C}{T} + \frac{10^{-6}DT^3}{3} \right) - \left( AT_0 + \frac{10^{-3}BT_0^2}{2} - \frac{10^5C}{T_0} + \frac{10^{-6}DT_0^3}{3} \right) \quad (2.4)$$

For the actual reaction, equation 1.2, studied throughout this thesis equation 2.2 has the form

$$\Delta H_R = -\Delta H_{B_2O_3} - 3\Delta H_{H_2O} + 2\Delta H_{H_3BO_3} \quad (2.5)$$

Table 2.2: Parameters to calculate the reaction enthalpy for the system  $B_2O_3/H_3BO_3$  [30].

Compound	$\nu_i$	$H^0$ $\frac{J}{mol}$	A $\frac{J}{molK}$	B $\frac{J}{molK^2}$	C $\frac{JK}{mol}$	D $\frac{J}{molK^3}$	$T_{min}$ K	$T_{max}$ K
$B_2O_3$ (s)	-1	-1271900	64.159	64.597	-18.365	0.033	298.150	723.000
$H_2O$ (l)	-3	-285830	186.884	-464.247	-19.565	548.631	273.151	495.000
$H_3BO_3$ (s)	2	-1094800	3.775	276.168	0.233	-3.551	298.150	444.100

The parameters needed to calculate the reaction heat are summarized in table 2.2. The result of this calculation can be seen in figure 2.1. According to this figure the produced heat increases for higher temperatures. Accordingly the needed energy for the reverse reaction also increases at higher temperatures.

### 2.1.6 Conversion calculations

Since no other characterization of the reaction progress is possible, the conversion will be calculated by the produced heat. In an adiabatic reactor the temperature continues to rise as long as a reaction occurs and heat is produced. When the reaction is finished, the temperature stays at a constant value. Considering the temperature elevation from the beginning of the reaction to the end it is possible to calculate the in total produced heat  $Q_R$ . Therefore it is first necessary to calculate the enthalpies at the end of the reaction of all occurring species. The index  $i$  describes the solvent,  $B_2O_3$ ,  $H_3BO_3$  and water.

$$H_i(t_{end}) = H_i^0 + \int_{T_0}^T c_{p,i} dT' \\ A_i T_{ad}(t_{end}) + 10^{-3} B_i \frac{T_{ad}(t_{end})^2}{2} - 10^5 C_i T_{ad}(t_{end})^{-1} + 10^{-6} D_i \frac{T_{ad}(t_{end})^3}{3} \\ - \left( A_i T(t_0) + 10^{-3} B_i \frac{T(t_0)^2}{2} - 10^5 C_i T(t_0)^{-1} + 10^{-6} D_i \frac{T(t_0)^3}{3} \right) \quad (2.6)$$

$t_{end}$  ... time when the reaction ends

$t_0$  ... time of reaction start

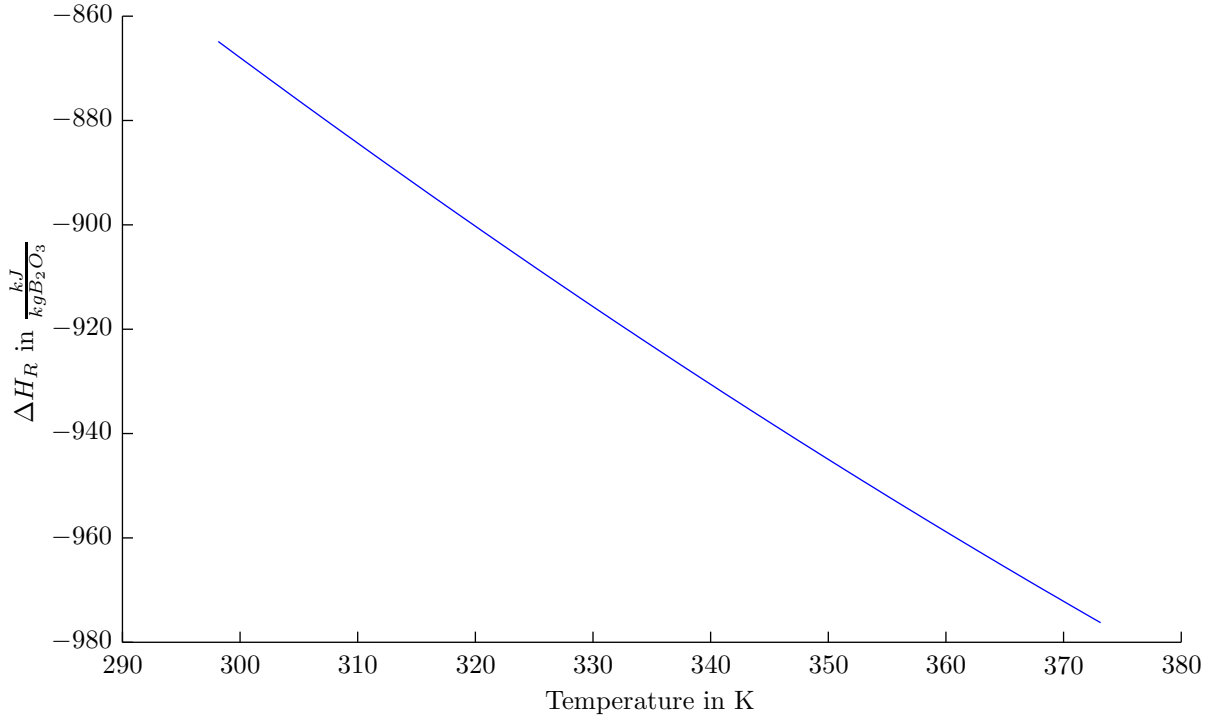


Figure 2.1: Reaction heat for the reaction of boron oxide and water to boric acid.

$T_{ad}$  ... temperature in adiabatic reactor

The molar masses at the end are also needed to be able to calculate  $Q_R$ . These molar masses are calculated by 2.7-2.9 if water was in excess and by 2.10-2.12 if boron oxide was in excess.

$$n_{B_2O_3}(t_{end}) = 0 \quad (2.7)$$

$$n_{H_3BO_3}(t_{end}) = 2n_{B_2O_3,0} \quad (2.8)$$

$$n_{H_2O}(t_{end}) = n_{H_2O,0} - 3n_{B_2O_3,0} \quad (2.9)$$

$$n_{B_2O_3}(t_{end}) = n_{B_2O_3,0} - n_{H_2O,0} \quad (2.10)$$

$$n_{H_3BO_3}(t_{end}) = \frac{2}{3}n_{H_2O,0} \quad (2.11)$$

$$n_{H_2O}(t_{end}) = 0 \quad (2.12)$$

The produced heat is then calculated by summing up all enthalpies for the different species multiplied with the corresponding molar masses.

$$Q_R = \sum_i (n_i(t_{end})H_i(t_{end})) \quad (2.13)$$

Since the totally produced heat was calculated, it is now possible to calculate the conversion at every time  $t$ . At  $t_0$  the conversion equals 0 since no reaction occurred yet. For every time-step afterwards the molar masses of the substances are calculated with the conversion from the previous time-step so it is not necessary to iterate.

If water is the species in excess the molar masses can be calculated by 2.14-2.16.

$$n_{B_2O_3}(t) = n_{B_2O_3,0}(1 - x(t - 1)) \quad (2.14)$$

$$n_{H_3BO_3}(t) = 2n_{B_2O_3,0}x(t - 1) \quad (2.15)$$

$$n_{H_2O}(t) = n_{H_2O,0} - 3n_{B_2O_3,0}x(t - 1) \quad (2.16)$$

Especially for cases, where a stoichiometric mixture between  $B_2O_3$  and water was applied, it was possible for boron oxide to be in excess. In these cases 2.17-2.19 apply

$$n_{B_2O_3}(t) = n_{B_2O_3,0} - n_{H_2O,0}x(t - 1) \quad (2.17)$$

$$n_{H_3BO_3}(t) = \frac{2}{3}n_{H_2O,0}x(t - 1) \quad (2.18)$$

$$n_{H_2O}(t) = n_{H_2O,0}(1 - x(t - 1)) \quad (2.19)$$

With this the enthalpies for each species can be calculated and following the heat produced until  $t$ .

$$H_i(t) = A_i T_{ad}(t) + 10^{-3} B_i \frac{T_{ad}(t)^2}{2} - 10^5 C_i T_{ad}(t)^{-1} + 10^{-6} D_i \frac{T_{ad}(t)^3}{3} - \left( A_i T_{ad}(t_0) + 10^{-3} B_i \frac{T_{ad}(t_0)^2}{2} - 10^5 C_i T_{ad}(t_0)^{-1} + 10^{-6} D_i \frac{T_{ad}(t_0)^3}{3} \right) \quad (2.20)$$

$$Q(t) = \sum_i n_i(t) H_i(t) \quad (2.21)$$

The conversion can now be calculated with  $Q$  and  $Q_R$  since it was assumed that the conversion directly corresponds with the produced heat.

$$x(t) = \frac{Q(t)}{Q_R} \quad (2.22)$$

Now it is possible to use the calculated conversion for the time  $t+1$ .

## 2.2 Material characteristics

### 2.2.1 Boron trioxide

Boron trioxide, only called boron oxide from now on, has the formula  $B_2O_3$ . Other names are diboron trioxide and boric acid anhydride. It is a white, hygroscopic powder. Normally it is found in the amorphous form. It has a molar mass of 69.6182 g/mol and a density of 2.55 g/cm<sup>3</sup>. The melting point of this substance is at 450 °C [31].

### 2.2.2 Boric acid

The most commonly used boric acid is the orthoboric acid. Boric acid is often found near fumaroles because the steam exiting them contains large amounts of it. For example in the suffioni of Tuscany the steam contains up to 0.5g of  $\text{H}_3\text{BO}_3$  per litre steam with pressures around 5 atm and temperatures of 190 °C. The ejected boric acid is forming the mineral sassolite [32]. Besides the orthoboric acid there are three crystal forms of metaboric acid [33].

#### Forms of boric acid

The formula of orthoboric acid is  $\text{B}(\text{OH})_3$  which leads to a molecular weight of 61.83 g/moles. When crystallizing it forms triclinic plates. Its melting point is 170.9 °C. If heated slowly some water is given off to yield  $\text{HBO}_2$  or metaboric acid with a molar mass of 43.82 g/moles [33].

#### Properties

The solubility of boric acid in water is greatly depending on the the temperature. Table 2.3 gives an overview over this dependency. The table also shows that boric acid lowers the melting point of water and increases the boiling point.

Table 2.3: solubility of boric acid in correlation to the temperature [33].

Temperature in °C	weight% $\text{H}_3\text{BO}_3$
-0.76 (melting point)	2.47
0	2.52
10	3.49
20	4.72
30	6.23
40	8.08
50	10.27
60	12.97
70	15.75
80	19.10
90	23.27
100	27.53
103.3 (boiling point)	29.27

Table 2.4 shows the solubility of boron trioxide in various solvents [33]. Some of these solvents, especially the alcohols are tending to react with boric acid to form borate esters. This is further explained in 2.2.4.

### 2.2.3 The boron oxide - boric acid system

It is possible to call boric acid a hydrate of boron oxide with the formula  $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  for orthoboric acid and  $\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$  for metaboric acid. If orthoboric acid is heated slowly, instead of melting it releases water to form orthorhombic  $\text{HBO}_2$  – III at around 80 °C and gradually changes to  $\text{HBO}_2$  – II up to 130 °C. Over 140 °C  $\text{HBO}_2$  – II converts to  $\text{HBO}_2$  – I

Table 2.4: solubility of boric acid in selected organic solvents [33].

Solvent	Temperature in °C	weight% H <sub>3</sub> BO <sub>3</sub>
Ethylene glycol	25	18.5
Diethylene glycol	25	13.6
Methanol	25	173.9 g/L solvent
Ethanol	25	94.4 g/L solvent
n-Propanol	25	59.4 g/L solvent
n-butanol	25	42.8 g/L solvent
Acetone	25	0.6 g/L solvent
Methyl ethyl ketone	20	0.7
Ethyl acetate	25	1.5

and above 200 °C HBO<sub>2</sub> – I transforms to B<sub>2</sub>O<sub>3</sub> [34]. The melting points are summarized again in table 2.5.

Figure 2.2 shows the stable modes of boron oxide depending on the temperature and mole fraction of B<sub>2</sub>O<sub>3</sub> in water. The curves describe the melting points of the mixtures.

Table 2.5: Melting points of boron oxide, all three modifications of metaboric acid and orthoboric acid [35].

Compound	melting point in °C
B <sub>2</sub> O <sub>3</sub>	450
HBO <sub>2</sub> – I	236
HBO <sub>2</sub> – II	201
HBO <sub>2</sub> – III	176
H <sub>3</sub> BO <sub>3</sub>	170.9

### The system B<sub>2</sub>O<sub>3</sub>/H<sub>3</sub>BO<sub>3</sub> as TCES

In the course of a research program on the Vienna University of Technology called "Solid-Heat" <sup>1</sup> a logarithm was developed in order to find currently unexploited materials, which are well suited for thermal energy storage [18]. To be selected as a promising material, several criteria have to be fulfilled. Some of these criteria are a high energy storage density and availability. One of the systems found with this algorithm was B<sub>2</sub>O<sub>3</sub>/H<sub>3</sub>BO<sub>3</sub>. According to its temperature range, it was classified as a low temperature energy storage.

Low temperature energy storages range from 0 - 120 °C [36], therefore including this system, since liquid water only is available between 0 and 100 °C. Some applications for this temperature range are space heating, hot water production, green house heating, solar cooling and many more [16, 36, 37].

#### 2.2.4 Boron esters

Boron esters have similar properties as other typical organic substances. Normally they are colourless liquids or white solids. They are soluble in organic solvents, combustible and volatile and generally melt below 400 °C. Water is not able to solute most of these compounds

<sup>1</sup><http://solidheat.project.tuwien.ac.at/>



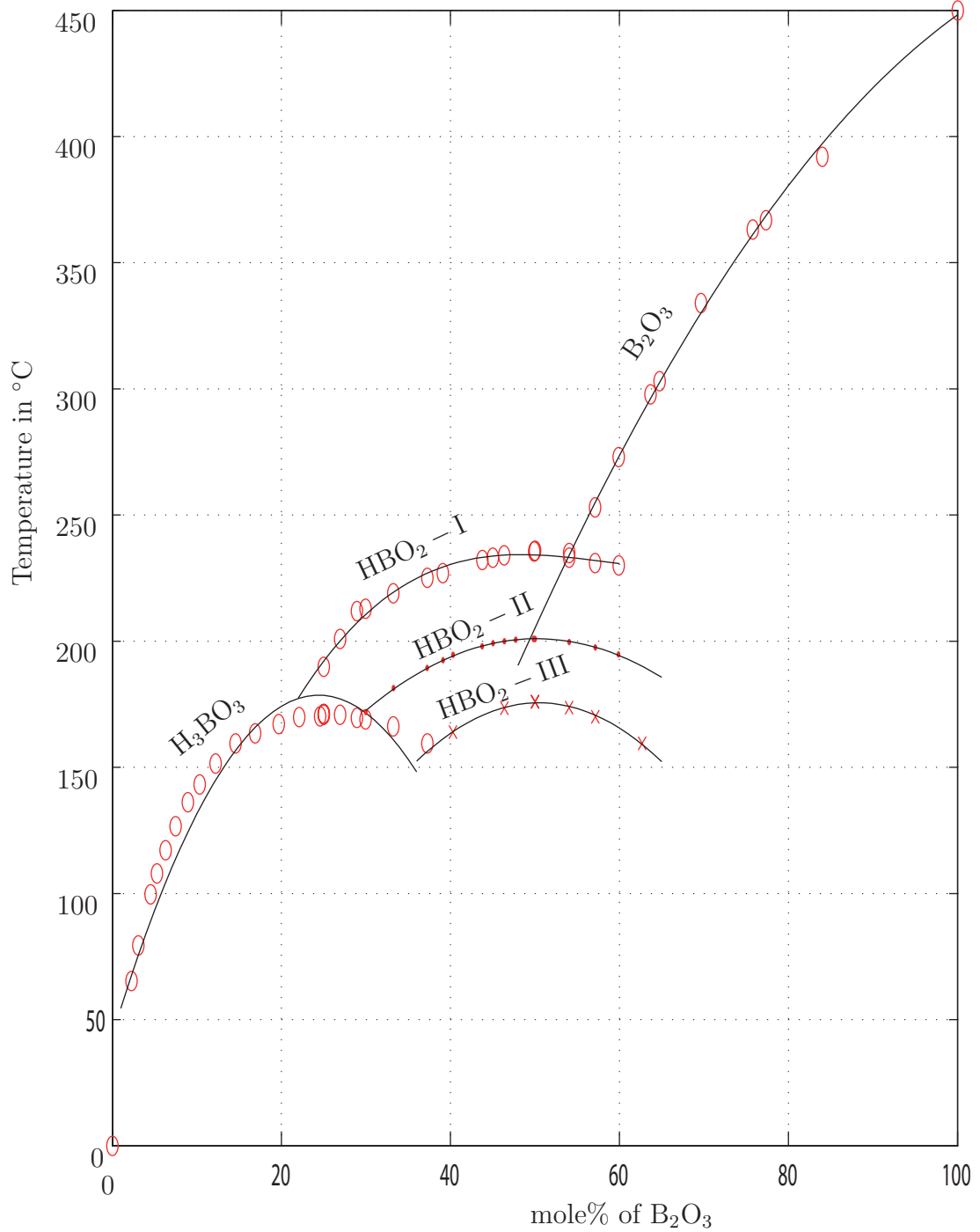


Figure 2.2: Solubility diagram for the system H<sub>2</sub>O - B<sub>2</sub>O<sub>3</sub>. Adapted from [32].

since it hydrolyses the material. Therefore they just appear to mix or dissolve when in reality they react with the water. This hydrolytic instability already leads to a decomposition when exposing the material to humidity in air [38].

### Symmetrical orthoborates of monohydric alcohols and phenols

Trialkoxyboranes and Triaryloxyboranes are the best known boron-oxygen compounds. Their molecular structures are depicted in figure 2.3.

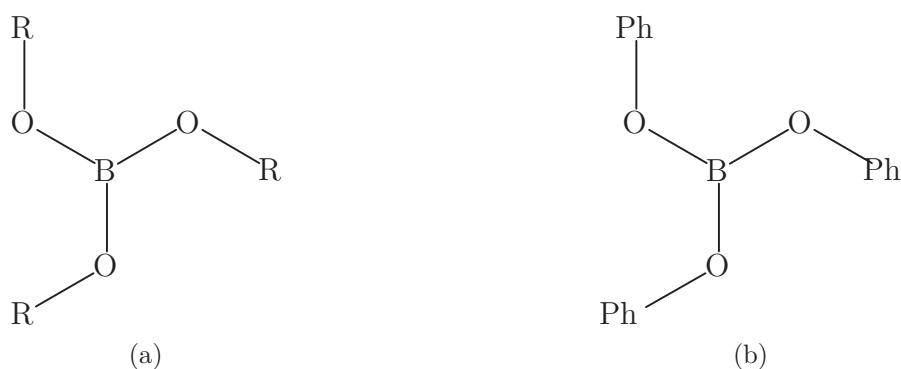


Figure 2.3: (a) depicts the structural formula of Trialkoxyboranes and (b) depicts the structural formula of Triaryloxyboranes [38].

Depending on the organic chain the substances range from volatile liquids to polymeric solids which decompose upon heating [38]. The boiling point of selected esters are collected in table 2.6. For comparison, the boiling points of the corresponding alcohols were also added. Observing the trend shows that the difference between the boiling points of the ester and the alcohol is increasing for longer chains.

Table 2.6: Molar mass and boiling point of various trialkoxyboranes adapted from [38].

R in $(RO)_3B$	molecular weight in g/mol	boiling point in $^{\circ}C$	boiling point of the corresponding alcohol in $^{\circ}C$
$CH_3$	104	68.5	64.7
$C_2H_5$	146	118	78.37
n- $C_3H_7$	188	177	97
n- $C_4H_9$	230	230	117.7

The esters normally have the same smell as the alcohols they are based on, this could be due to the hydrolysis occurring at ambient conditions. Most of the esters are soluble in organic solvents but not soluble in water [38].

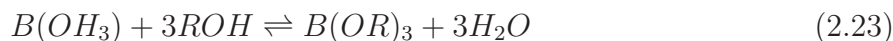
Considering their structure borate esters were sometimes called ethers but if their reactivity towards hydrolysis, alcoholysis, etc. is taken into account they are more comparable to esters [38].

### Preparation of borate esters

**From boric acid** Most of the times the esters are prepared from boric acid and an alcohol or phenol. The occurring reaction can be seen in equation 2.23.

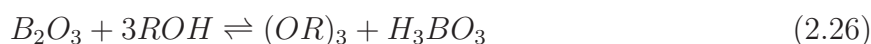
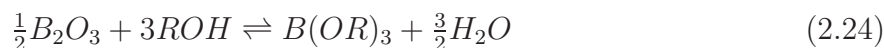
Table 2.7: Heat of formation for trimethyl borate and triethyl borate

	reaction	reaction heat in kJ/kg $B_2O_3$
trimethyl borate	$B_2O_3 + 3CH_3OH \rightleftharpoons B(OCH_3)_3 + H_3BO_3$	-584.72 [30]
triethyl borate	$B_2O_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + H_3BO_3$	-622.55 [38]



The equilibrium of this reaction lies close to the educts. Therefore either the ester or the water have to be removed. Depending on the formed ternary mixture consisting of water, alcohol and ester it might prove difficult to remove either the water or the alcohol. To overcome the often formed azeotropes an excess of alcohol is added which is distilled together with water. Sadly, especially for methanol and ethanol this approach cannot be used since they form a lower boiling azeotrope with their ester than with water [38].

**From boron oxide** If boron oxide is used in an excess of 100% then the water produced during the esterification is consumed by this excess boron oxide. Therefore, 50% of the used boron oxide is not contributing to the conversion but reacts to boric acid according to equations 2.24 and 2.25. Combining equations 2.24 and 2.25 gives equation 2.26.



If the boric acid is not removed before distillation further reactions occur and meta- and polyborate could be formed. Especially for the lower boiling alcohols this approach proves simple. The mixture is heated, boric acid is removed by filtration and the filtrate is distilled to obtain the ester. The only downside is the loss of half of the boron as boric acid but if that is economically feasible then this approach is better than the more time consuming ternary azeotrope method further described in [38].

If the production of boric ester is not feasible the produced water has to be removed. Therefore six moles of alcohol have to be mixed with one mole of boron oxide according to equation 2.27. The water can be removed by generating a binary azeotrope with benzene or toluene.



Table 2.7 shows the reaction and the heat of formation at standard conditions for the two simplest boron esters formed with boron oxide.

### Hydrolytic stability

If a borate ester gets into contact with water, either through water or moisture in the air it normally reacts back to boric acid and alcohols. Only some sterically hindered esters are

rather stable concerning water. The reaction occurring during hydrolysis is the following one



### Orthoborates derived from dihydric alcohols and phenols

If dihydric alcohols are used for boronate esters various different structures are possible. They can either form structure a or b in figure 2.4, the two monomeric forms or they form a polymer with various possible structures. Figure 2.4c gives one possible structure for such polymer.

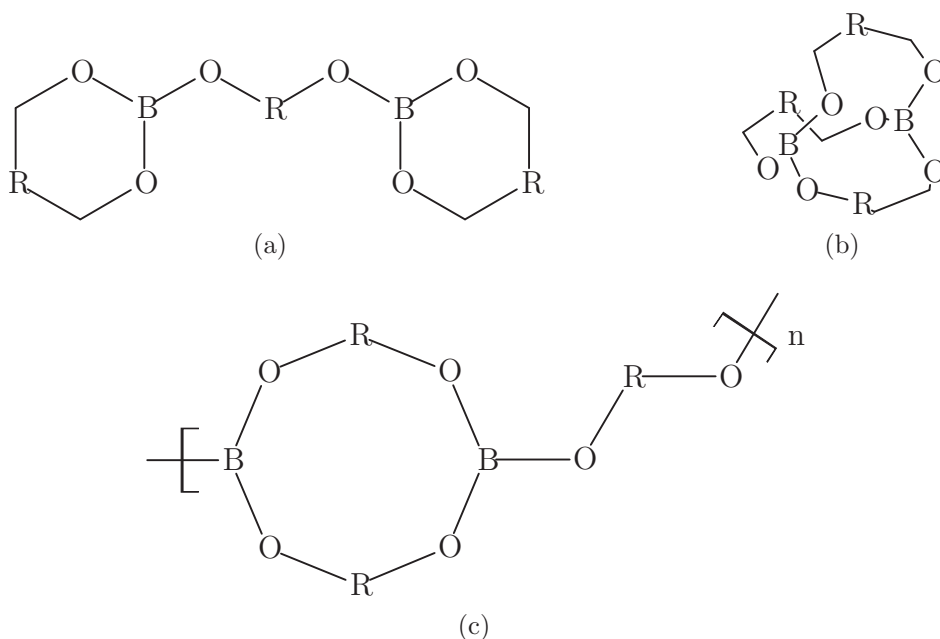


Figure 2.4: (a) and (b) depict the two possible structures of monomeric trialkoxyboranes. (c) depicts one possible structure of a polymer [38].

This esters can be prepared in the same way as using monohydric alcohols as described above.

### 2.2.5 Solvent literature study

Since the reaction is to be studied in a solvent, it was necessary to evaluate a first list of possible candidates. Therefore various solvents were researched, which are listed in table 2.9 and table 2.8. Various aspects of these solvents were gathered and compared to quantify the potential of these solvents. The aspects studied included the boiling point, the heat capacity, safety and health hazards and the price.

Following these tables, triethylene glycol, methanol, ethanol, acetone, ethyl acetate, heptane and methyl isobutyl ketone were chosen for this study. Triethylene glycol was chosen as representative of the glycols, since it was readily available and methanol and ethanol were chosen as the other studied alcohols since they are the two simplest ones. Acetone and ethyl acetate were chosen since they are commonly used solvents in laboratories. Heptane and

Table 2.8: hazards of various solvents

Solvent	hazards [39]
Glycerin	none
Dimethyl sulfoxide (DMSO)	none
Ethylene glycol	Harmful if swallowed
Triethylene glycol	none
propylene glycol	none
Xylene	Flammable liquid and vapour Harmful in contact with skin Causes skin irritation Harmful if inhaled
Chlorobenzene	Flammable liquid and vapour Harmful if inhaled Toxic to aquatic life with long lasting effects
Propylene carbonat	May cause an allergic skin reaction Causes serious eye irritation Very toxic to aquatic life Very toxic to aquatic life with long lasting effects
Diethylene glycol	Harmful if swallowed Causes damage to kidneys if swallowed May cause drowsiness and dizziness
Methanol	Highly flammable liquid and vapour Toxic if inhaled Toxic in contact with skin Toxic if swallowed Causes damage to organs. Affected organs: eyes
Ethanol	Highly flammable liquid and vapour Causes serious eye irritation
Acetone	Highly flammable liquid and vapour Causes serious eye irritation May cause drowsiness or dizziness
Ethyl acetate	Highly flammable liquid and vapour Causes serious eye irritation May cause drowsiness or dizziness
Heptane	Highly flammable liquid and vapour May be fatal if swallowed and enters airways Causes skin irritation May cause drowsiness or dizziness Very toxic to aquatic life with long lasting effects
Methyl isobutyl ketone	Highly flammable liquid and vapour Harmful if inhaled May cause respiratory irritation H319: Causes serious eye irritation

Table 2.9: boiling point, water miscibility and price of selected solvents

Solvent	boiling point in °C [40]	water miscible [40]	price in €/g taken from <sup>2</sup>
Glycerin	290	yes	0.033
Dimethyl sulfoxide (DMSO)	189	yes	0.019
Ethylene glycol	195	yes	0.010
Triethylene glycol	285	yes	0.025
propylene glycol	188.2	yes	0.010
Xylene	138.5	practically insoluble	0.015
Chlorobenzene	131	0,5g/L water	0.007
Propylene carbonat	242	yes	0.003
Diethylene glycol	246	yes	0.010
Methanol	64.7	yes	0.020
Ethanol	78.29	yes	0.018
Acetone	56.08	yes	0.012
Ethyl acetate	77.1	64 g/L at 25 °C	0.012
n-Heptane	98.38	3.4 mg/L at 25 °C	0.011
Methyl isobutyl ketone	117-118	19 mg/L at 25 °C	0.015

Table 2.10: Standard enthalpy of formation and parameters to approximate  $c_p$  for various solvents taken from HSC database [30].

Compound	$H^0$	A	B	C	D	$T_{min}$	$T_{max}$
	$\frac{J}{mol}$	$\frac{J}{molK}$	$\frac{J}{molK^2}$	$\frac{JK}{mol}$	$\frac{J}{molK^3}$	K	K
TEG	-819.462	339.661	0	0	0	298.15	300.00
methanol	-238.697	157.390	-637.206	-4.289	1327.098	298.15	337.60
ethanol	-276.981	124.905	-440.056	-0.770	1359.101	173.00	351.30
acetone	-258236	-224.565	1879.637	76.794	-2034.566	273.15	333.15
acetone	0	-224.565	-2330.766	-111.351	2773.527	333.15	473.15
ethyl acetate	-44500	23.175	350.891	-4.121	-139.850	298.15	1100.00
heptane	-224388	224.723	0	0	0	298.15	371.07
MIBK	-328400	209.600	0	0	0	298.15	300.00

methyl isobutyl ketone were selected since their boiling point is close to the one of water. The other solvents were not studied, since they were not already available or they posed unnecessary dangers to human health or the environment.

## 2.2.6 Solvents

The solvents used throughout this study are shortly characterised in the following. Table 2.10 summarizes the standard heats of formation and the parameters to approximate the  $c_p$  value for all the solvents used. For some solvents the used range exceeded the range of the parameters, but they were used regardless since no other data was available.

One of the main aims of this work is to increase the maximal reachable temperature during the reaction of boron oxide to boric acid. Therefore some of the water is substituted by a

<sup>2</sup><http://db.chemie.tuwien.ac.at/search/>

Table 2.11: Heat capacity for various solvents at 25 °C [30].

solvent	heat capacity in $\frac{\text{kJ}}{\text{kgK}}$
triethylene glycol	1.3946
methanol	2.5140
ethanol	2.4670
acetone	4.1560
ethyl acetate	1.2567
heptane	2.2427
methyl isobutyl ketone	2.0927
water	4.1759

solvent with a lower  $c_p$ -value than water. Table 2.11 summarizes these values and shows, that all the chosen solvents have a lower heat capacity than water.

### Triethylene glycol

Triethylene glycol, in the following TEG, is a viscous, odourless and colourless liquid. It consists of three ethylene glycol units connected by releasing water to form an ether with two hydroxyl groups left. It has the chemical formula  $\text{C}_6\text{H}_{14}\text{O}_4$  and a molar mass of 150.17 g/mol. Its density is 1.1255 g/mL and it has a boiling point of 285 °C. Figure 2.5 shows the heat of mixing for the system water-TEG. Since all the values are negative, heat is released when the two substances are mixed.

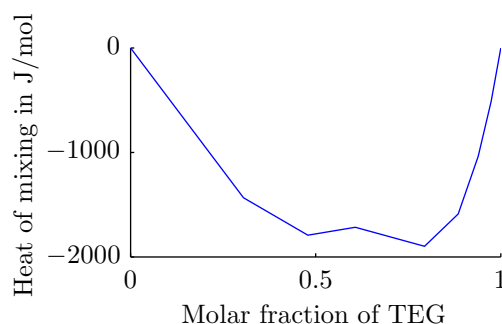


Figure 2.5: Heat of mixing of water and triethylene glycol [41].

### Methanol

Methanol is a volatile, colourless liquid, with a similar odour to ethanol. It has the formula  $\text{CH}_3\text{OH}$  with a molar mass of 32.04 g/mol. The boiling point of methanol is 64.7 °C and it is miscible with water. Its density is 0.792 g/mL. The vapour-liquid equilibrium of methanol and water can be seen in figure 2.6a and the heats of mixing in figure 2.6b.

### Ethanol

Ethanol has the chemical formula  $\text{C}_2\text{H}_5\text{OH}$  and it has a molar mass of 46.07 g/mol. It is a volatile, flammable and colourless liquid with a typical odour. Its density is 0.789 g/mL at 20 °C, it has a boiling point of 78.37 °C and is miscible in water. The vapour-liquid equilibrium with water can be seen in figure 2.7a and the resulting heat of mixing, when

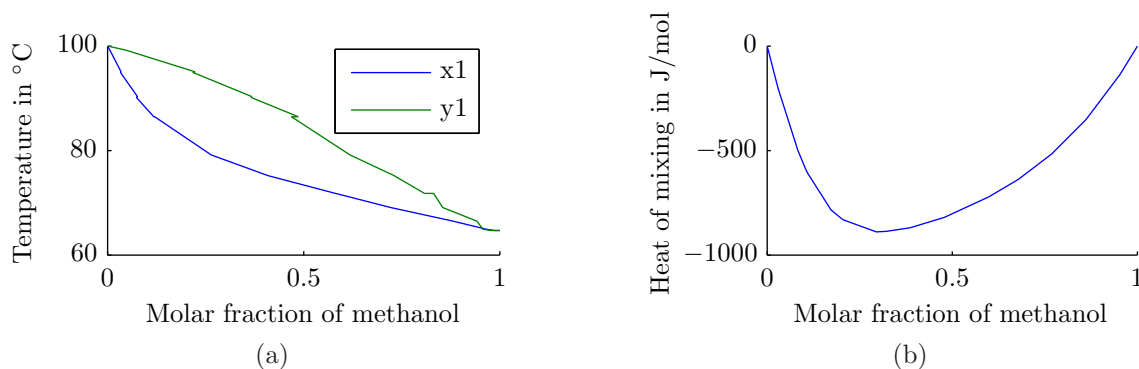


Figure 2.6: (a) shows the vapour-liquid equilibria for the system methanol-water [42] (b) depicts the heat of mixing of the system methanol-water [43].

mixing those two in figure 2.7b. Figure 2.7a also shows an azeotropic point around a molar fraction of 0.9 of ethanol with a boiling point of 78.1 °C, which is below the boiling point of both substances alone.

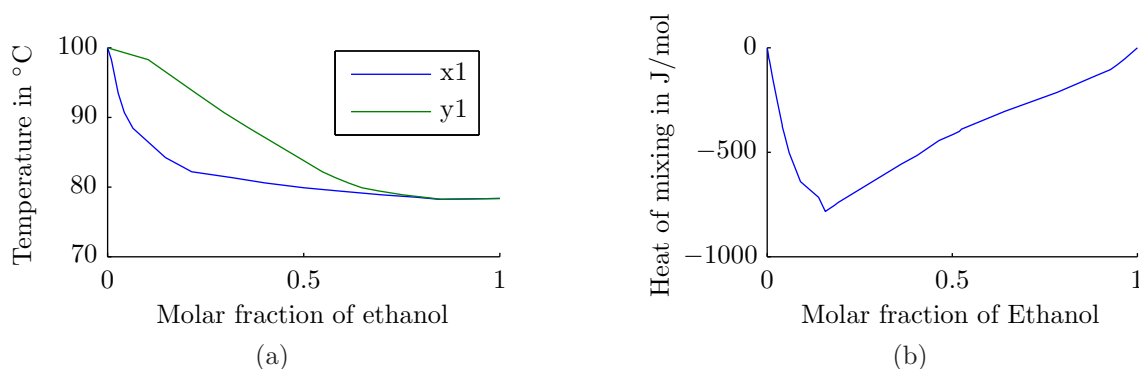


Figure 2.7: (a) shows the vapour-liquid equilibria for the system ethanol-water [44] (b) depicts the heat of mixing of the system ethanol-water [45].

### Acetone

Acetone, with the systematic name propanone, is the simplest ketone with the chemical formula  $C_3H_6O$  and a molar mass of 58.08 g/mol. It is a volatile, flammable, colourless liquid. Its density is 0.7845 g/mL at 25 °C and it has a boiling point of 56.05 °C. With water it is miscible which can be seen in figure 2.8b. Furthermore, figure 2.8a shows the vapor-liquid equilibrium for those two substances.

### Ethyl acetate

Ethyl acetate is the ester of acetic acid and ethanol, it has the chemical formula  $C_4H_8O_2$  and a molar mass of 88.11 g/mol. It is a colourless, volatile solvent with a characteristic sweet smell. The density of ethyl acetate is 0.902 g/mL and its boiling point is 77.1 °C. Water and ethyl acetate are only partly miscible, as can be seen in figure 2.9, with the solubility of ethyl acetate decreasing for higher temperatures and the solubility of water increasing when the temperature rises.



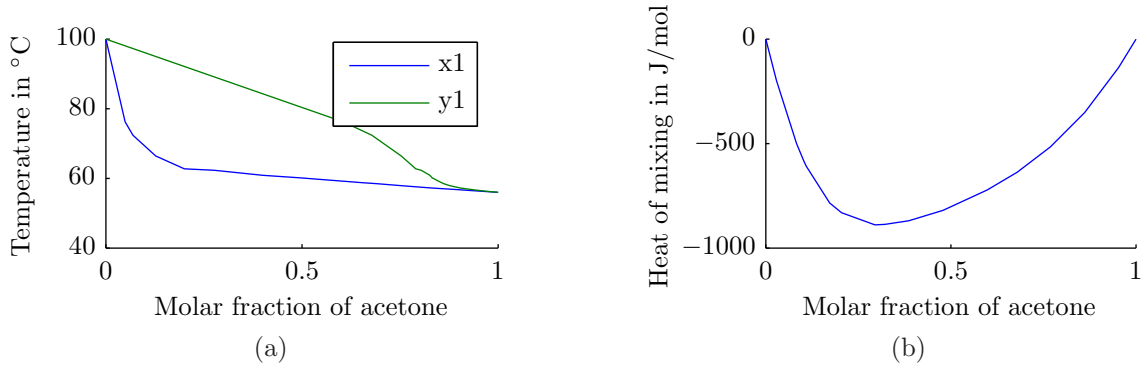


Figure 2.8: (a) shows the vapour-liquid equilibria for the system acetone-water [46] (b) depicts the heat of mixing of the system acetone-water [45].

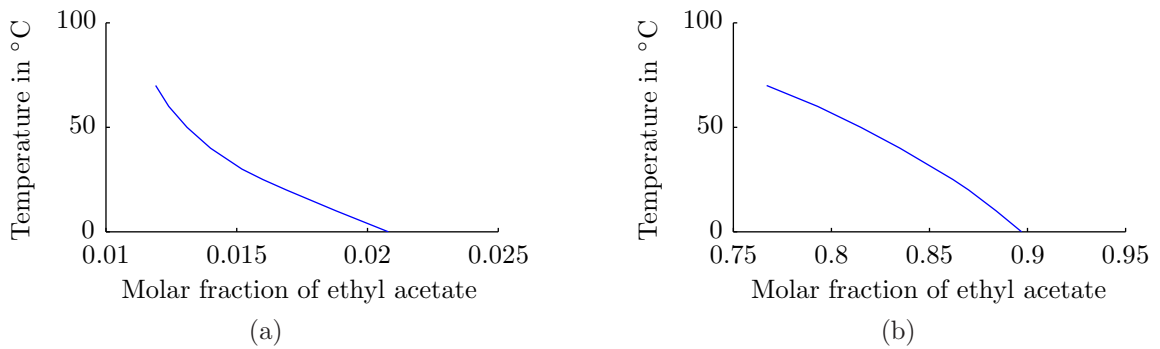


Figure 2.9: (a) depicts the solubility of ethyl acetate in water and (b) the solubility of water in ethyl acetate. The solubilities were taken from [47].

The vapor-liquid equilibrium is depicted in 2.10a and the heat of mixing, which is depicted in figure 2.10b. In this figure it is visible, that the mixing changes from an exothermal process for small ethyl acetate amounts to an endothermal process for high ethyl acetate concentrations.

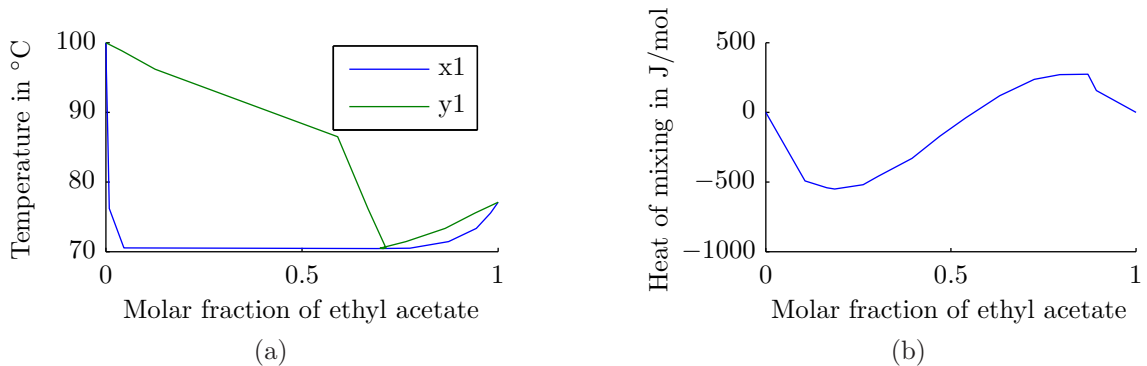


Figure 2.10: (a) shows the vapour-liquid equilibria for the system ethyl acetate-water [48] (b) depicts the heat of mixing of the system ethyl acetate-water [49].

## n-Heptane

n-Heptane is the straight alkane with the formula  $C_7H_{16}$  and a molar mass of 100.21 g/mol. It is a colourless liquid with a petrolic odour. In the octane rating scale it is used as reference for the zero point. The boiling point of heptane is 98.38 °C and the density is 0.6795 g/mL. This solvent is nearly immiscible in water, figure 2.11 gives an overview over the miscibility of heptane in water and water in heptane.

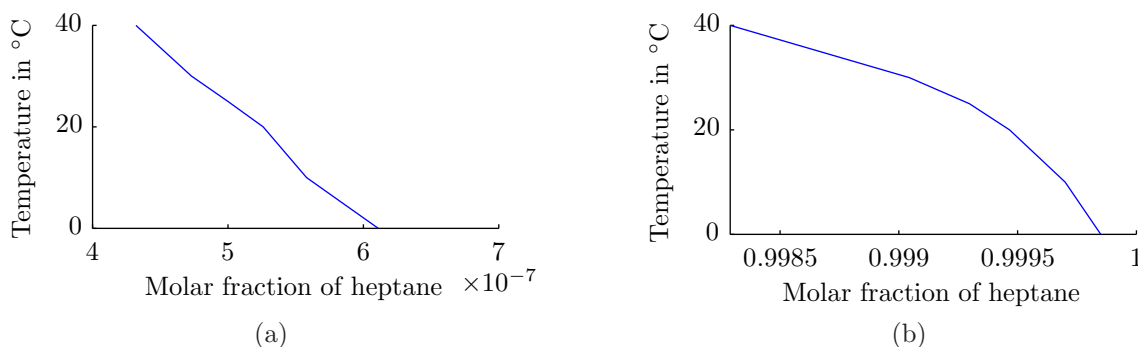


Figure 2.11: (a) depicts the miscibility of heptane in water and (b) the miscibility of water in heptane [47].

## Methyl isobutyl ketone

Methyl isobutyl ketone, in the following abbreviated with MIBK, also known as 4-methylpentan-2-one is a colourless liquid. The chemical formula is  $C_6H_{12}O$  and its molar mass is 100.16 g/mol. It has a density of 0.802 g/mL and a boiling point of 116.5 °C. This solvent is nearly immiscible in water with a miscibility of  $3.43 \cdot 10^{-3}$  mole fraction of MIBK in water and a mole fraction of 0.1 of water in MIBK [47].

## 2.3 Analytical methods

### 2.3.1 XRD

X-ray crystallography is used to identify the atomic and molecular structure of a crystal. The crystals diffract X-rays into many directions and by measuring the angles and intensities of the diffracted beams it is possible to obtain the crystal structure.

When a crystal is placed on a photographic film, an X-ray diffraction pattern can be obtained. This pattern consists of regularly spaced maxima, whose positions depend on the size of the unit cell and the crystal orientation. This can be calculated by considering the geometrical conditions for reflection on a series of lattice planes. Constructive interference can only occur when the parallel diffracted waves display a path difference of  $\lambda(2\pi)$  to their nearest neighbours. The Bragg equation:

$$\lambda = 2d_{hkl}\sin\theta \quad (2.29)$$

relates the wavelength  $\lambda$  to the interplanar distance  $d_{hkl}$  and the Bragg angle  $\theta$  [50].

### 2.3.2 NMR spectroscopy

NMR spectroscopy or nuclear magnetic resonance spectroscopy measures the magnetic properties of certain atomic nuclei. This method is based on nuclear magnetic resonance and is able to provide detailed information about the structure, dynamics, reaction state and chemical environment of molecules. The surroundings of the measured molecule influence the resonance frequency, therefore giving information about the structure of a molecule [50].

### 2.3.3 Karl-Fischer titration

Karl-Fischer titration is a classic titration method that uses coulometric or volumetric titration to determine trace amounts of water ranging from a few ppm to some weight% in a sample. Today the titration is done with automatized Karl-Fischer titrators [51].



# Chapter 3

## Methods

### 3.1 Experimental setup

The reactor used consisted of a three-necked flask, a dimroth cooler with a glove as pressure compensation attached to it, a stirrer with a mixing shaft and a mixing blade. Attached on the last neck of the bottle was a septum pierced with a thermal element, which measured the temperature of the mixture inside the flask. A second thermal element measured the ambient temperature. Both elements were connected to a PC and the data was recorded using LabVIEW. A detailed picture of the experimental setup can be seen in figure 3.1.

A closed reactor was chosen since the first used solvent, TEG, absorbed water from the surrounding air. To obtain sufficient mixing, a mixing shaft with a stirring blade was used. The cooler was added, since the reaction heat lead to the partial vaporisation of the mixture if a lower boiling solvent, e.g. acetone was used. An insulation was not installed since one of the aspects studied throughout this thesis was the behaviour and miscibility of the system at all times. An insulation would cover the parts studied and make a visual study of the system impossible.

### 3.2 Heat loss measurements

For the evaluation of the conversion, heat loss measurements were also needed. Therefore MIBK was heated in the reactor inside a water bath and taken out as soon as the measurement started. The temperature was measured until MIBK reached room temperature to cover the whole observed temperature range during the experiments.

The heat losses also had to be calculated for a second reactor used for comparisons with the work from Hashemi [20]. Therefore water was heated and filled into the reactor when it started boiling. The rest of the evaluation is the same as mentioned before for the other reactor.

Using the data obtained in the heat loss experiments it is possible to calculate the heat loss per time unit. Before that the temperature signal of the heat loss experiment is corrected using the form

$$T = ae^{-bt} + c \quad (3.1)$$

The values for a, b and c were evaluated by fitting a curve into the measurement. Since the heat loss is bigger at higher temperatures it was necessary to prioritize the data points at



(a) experimental setup



(b) detailed view of the three-necked flask

Figure 3.1: (a) The stirring unit consists of a stirring motor and a mixing shaft with a mixing blade. Additionally, there is a cooler with a glove attached to it as pressure compensation. On the other side of the three-necked flask is a thermal element attached through a septum. (b) shows a detailed view of the used three-necked flask with all the attachments added to it.

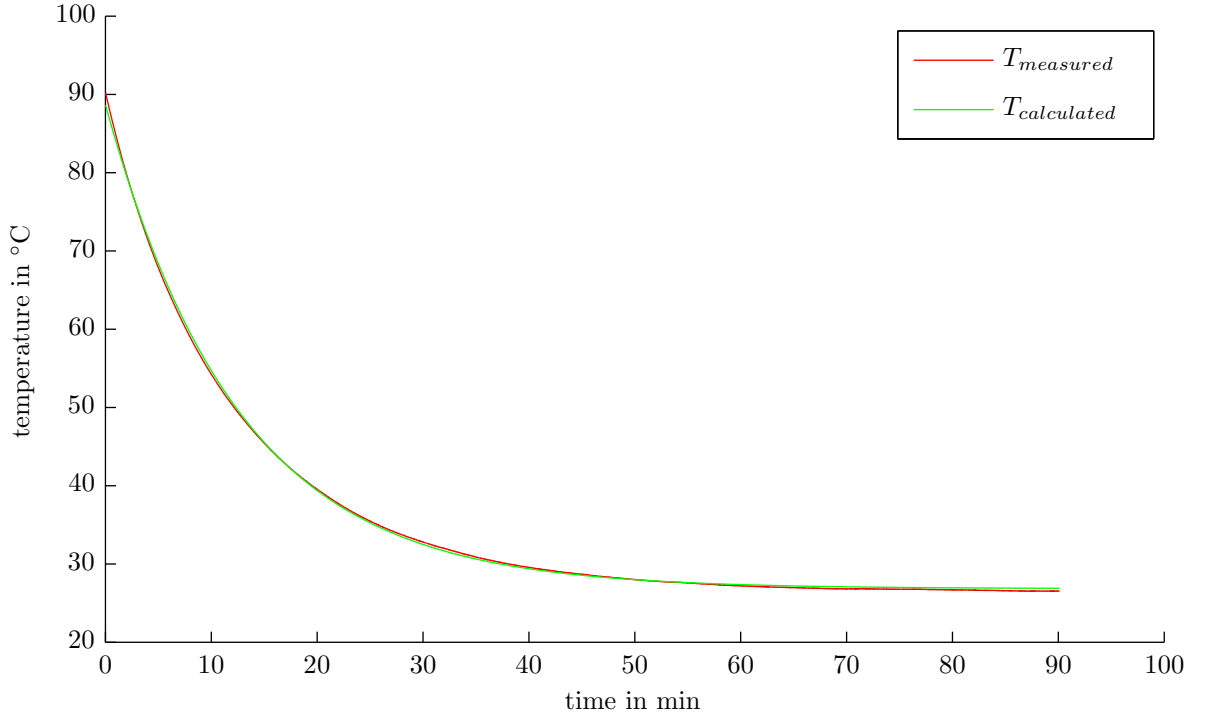


Figure 3.2: Comparison between the measured and the approximated decreasing temperature in the normal reactor.

higher temperatures by higher weighting them compared to data points at lower temperatures.

The heat loss experiments lead to the parameters summarized in table 3.1. Fitting the curve lead to high adjusted  $R^2$ , which is proving the correctness of the approximation. The temperature calculated by equation 3.1 with the values from table 3.1 lead to figures 3.2 and 3.3.

Table 3.1: Parameters to approximate the heat loss curves.

	a in K	b in 1/s	c in K	adjusted $R^2$
heat loss in normal reactor	61.88	0.00133	300	0.9996
heat loss in Hashemi's reactor	63.99	$1.954 \cdot 10^{-5}$	300.8	0.9988

With the smoothed temperature signal it is possible to calculate  $\dot{q}_{loss}$  according to equation 3.2.

$$\dot{q}_{loss}(t) = n_{MIBK} \left( \frac{AT(t) + 10^{-3}B\frac{T(t)^2}{2} - 10^5CT(t)^{-1} + 10^{-6}D\frac{T(t)^3}{3}}{t - (t+1)} - \frac{AT(t+1) + 10^{-3}B\frac{T(t+1)^2}{2} - 10^5CT(t+1)^{-1} + 10^{-6}D\frac{T(t+1)^3}{3}}{t - (t+1)} \right) \quad (3.2)$$

The values for  $A$ ,  $B$ ,  $C$  and  $D$  are  $A_{MIBK}$ ,  $B_{MIBK}$ ,  $C_{MIBK}$ , and  $D_{MIBK}$  respectively. The calculated heat losses can be interpolated to the measured temperatures.

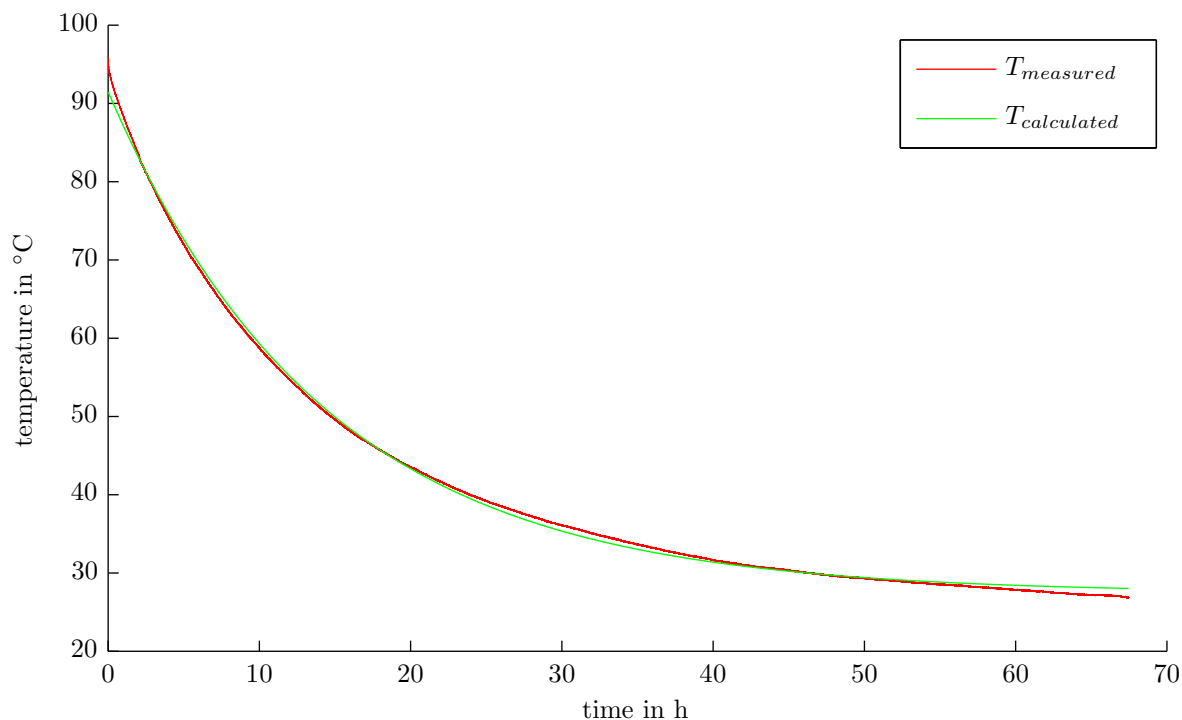


Figure 3.3: Comparison between the measured and the approximated decreasing temperature in Hashemi's reactor.

The heat loss calculated by equation 3.2 is depicted in figure 3.4 and increases linearly with temperature. It is visible, that the heat loss in the normal reactor is around five times higher than in Hashemi's reactor. Therefore this reactor is less advantageous in this regard, but it is closed so no fluid can evaporate and also it is possible to observe the reactions, which were chosen as more important aspects in this work.

### 3.3 Comparison measured temperature - corrected temperature

The heat loss encountered from the reactor to the surroundings was considered as described in 3.2. Figure 3.5 shows the adiabatic temperature and the measured temperature. The difference between the temperatures is minimal in the beginning of the reaction. Later on the difference increases with the measured values going down again and the corrected values still rising. The adiabatic temperature should reach a constant value in the end, which is not the case. This could either be because the reaction did not finish yet or because the heat losses occurring are less than were calculated.

The conversion for the case without correction was calculated by setting  $\dot{q}_{loss}=0$  J/s for all measurement points and then following the calculations 2.7-2.22. As with the temperatures, the conversion curves also overlap each other in the beginning and later on they diverge. Figure 3.6 shows this behaviour. The discrepancy between those values shows that the correction done throughout this work was really necessary.



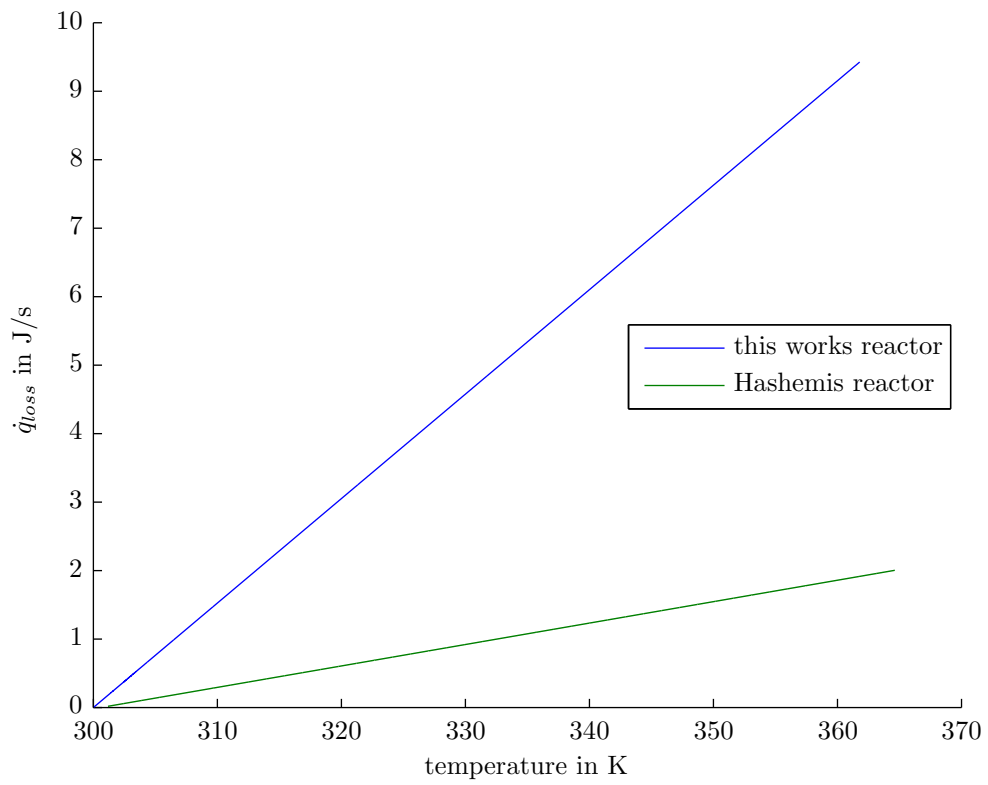


Figure 3.4: Heat loss in normal reactor and Hashemi's reactor.

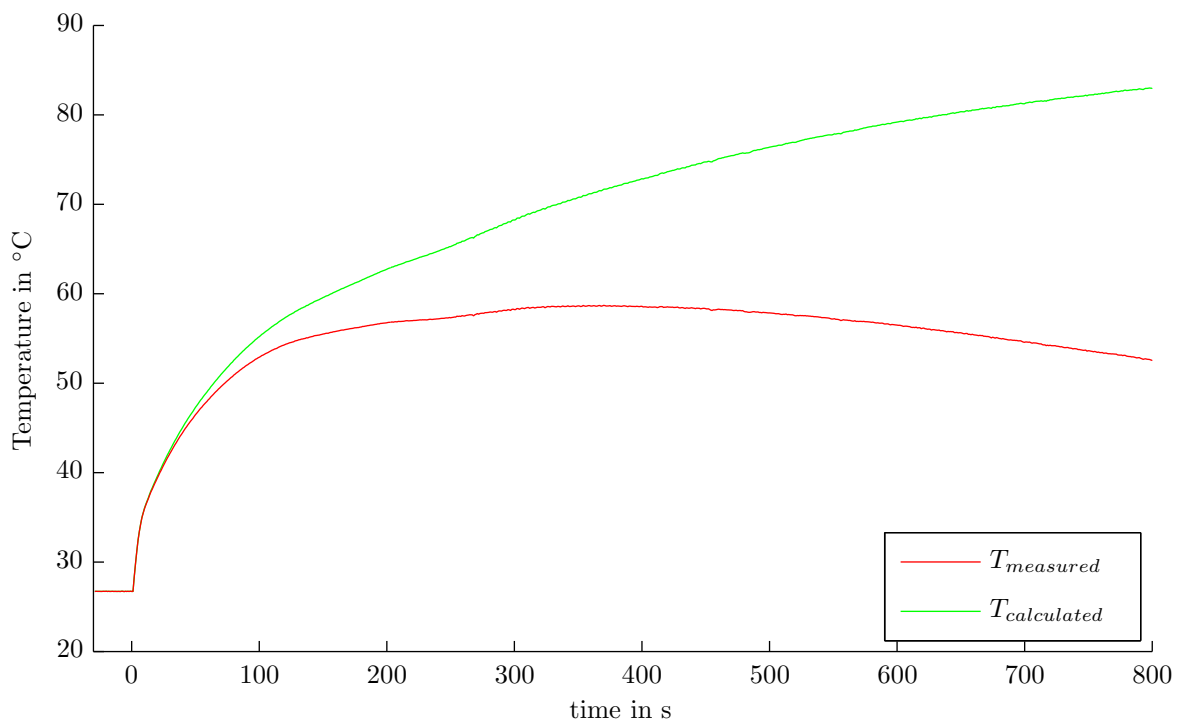


Figure 3.5: Difference between the measured temperature and the adiabatic temperature corrected with heat losses.

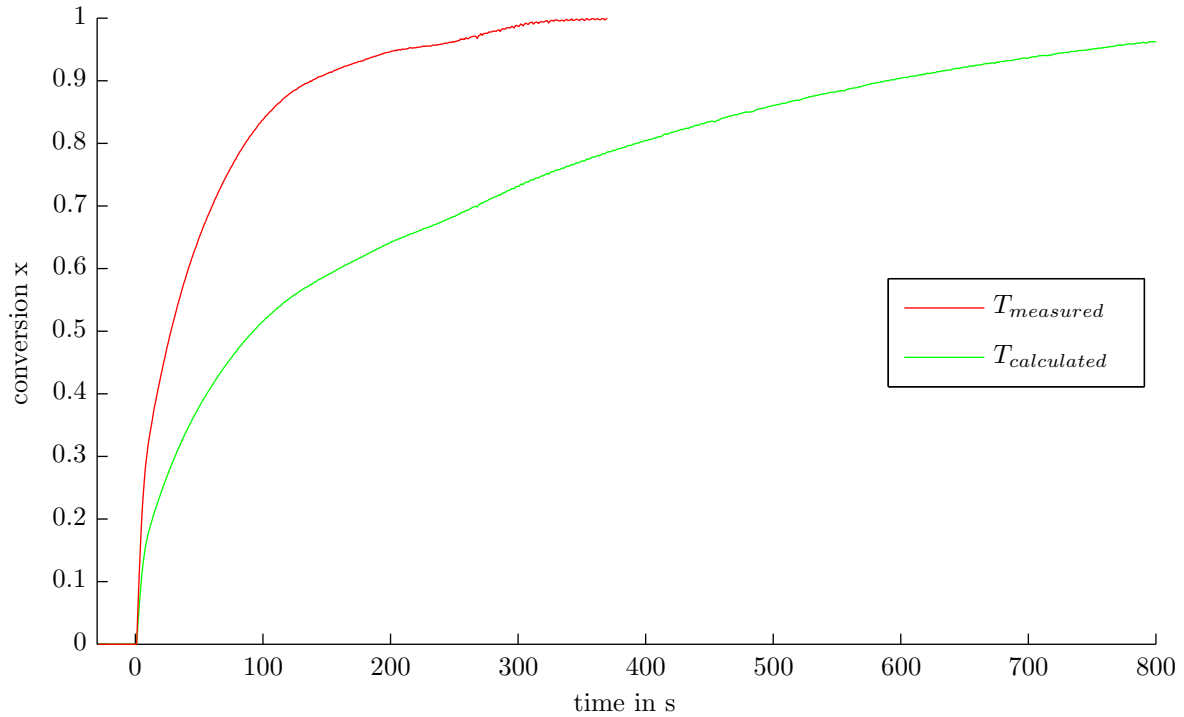


Figure 3.6: Compares the conversion calculated with the measured temperature with the conversion calculated with the corrected temperature.

### 3.4 Particle size distribution

A sieve analysis was conducted for every batch of boron oxide that was used. First of all, all the sieves were weighted empty and assembled so that the biggest sieve was at the top and the smallest sieve at the bottom. The boron oxide was added into the sieve column and the column was put into a Retsch Vibro mechanical shaker with 250 W. The sample was shaken for 13 minutes with a power of 60%. After that the single sieves were weighted again and the difference accounted for the material with this certain particle size.

Three batches were sieved. One batch BCBN9913V was from Sigma-Aldrich and the other two were from Alfa Aesar with the batch numbers R19A065 and Q13B026. The mass density distribution can be seen in figure 3.7 and the mass sum distribution in figure 3.8. The lot from Sigma-Aldrich has the maximum of the mass density distribution at a smaller particle size than the lots from Alfa Aesar. Therefore this boron oxide was only used for test experiments and not for the ones accounted for in this thesis. Both batches from Alfa Aesar have their maxima for the same particle size and were therefore both used for the experiments. Since the particle size was not further accounted for in this work, the differences for the batches was not further considered in this thesis.

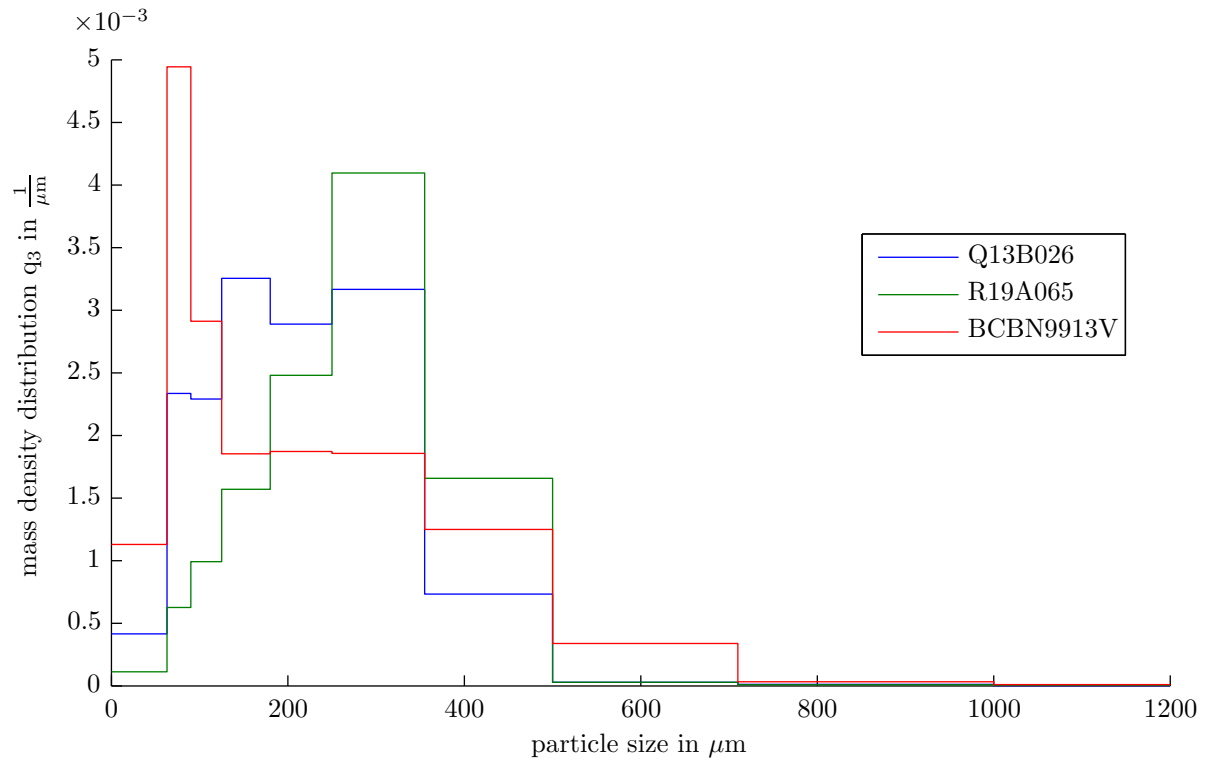


Figure 3.7: Mass density distribution for different batches of boron oxide

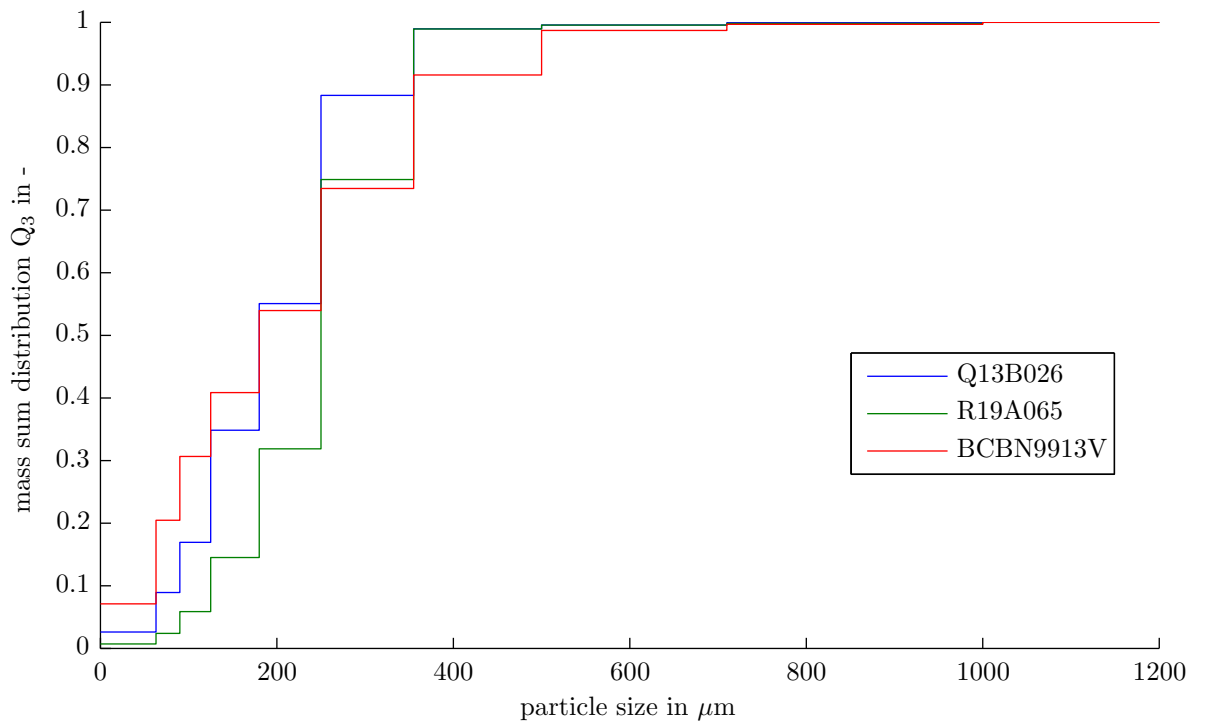


Figure 3.8: Mass sum distribution for different batches of boron oxide

## 3.5 Analysis

### 3.5.1 XRD

A product after the reaction in MIBK was dried and studied in an XRD. The powder X-ray diffraction measurement was carried out on a PANalytical X'Pert Pro diffractometer in Bragg-Brentano geometry using Cu  $K\alpha_{1,2}$  radiation and an X'Celerator linear detector with a Ni-filter. The diffractogram was evaluated using the PANalytical program suite HighScorePlus v3.0d. A background correction and a  $K\alpha_2$  strip were performed.

### 3.5.2 NMR

NMR studies were conducted for three different mixtures in MIBK. One was boric acid in MIBK, one was the reaction product and one was unreacted boron oxide. All spectra were recorded in dry, deuterated solvents as indicated.  $^{11}\text{B}$  spectra were recorded on a Bruker Avance UltraShield 400 MHz FT NMR spectrometer. All NMR chemical shifts are reported in ppm;  $^{11}\text{B}$  shifts are established on the basis of the residual solvent resonance.

### 3.5.3 Karl-Fischer-Titration

To be able to determine the total conversion after the reaction occurred it was necessary to measure the water content in the solvent before and after the reaction in a Karl-Fischer titrator. The titrator used was able to measure water in all solvents except for aldehydes and ketones. Measuring water contents of non-polar solvents proved difficult since the sample introduced did not have the same concentration as the studied solution. This was observed since samples that were supposed to have several weight% of water were measured with around 100ppm water.

The stirrer in the titrator was set to a speed of 5 and a delay of 1 minute was chosen. Depending on the expected water content 3-15 drops were added to obtain the ideal measure time of approximately 5 minutes. The water content was either given in ppm or weight% depending on the observed concentration.

## 3.6 Calculations

### 3.6.1 Total conversion calculations for the reaction $\text{B}_2\text{O}_3$ to $\text{H}_3\text{BO}_3$

To be able to calculate the total conversion of the reaction from boron oxide to boric acid the water content before (index 1) and after (index 2) the reaction is necessary.

Since the solvent does not react, the amount of pure solvent stays constant but the total amount of weighted solvent also includes the water in the solvent.

$$m_{\text{solvent},1} = m_{\text{solvent},2} = m_{\text{solvent}} \quad (3.3)$$

$$m_{\text{total},1} = m_{\text{solvent}} + m_{\text{H}_2\text{O},\text{solvent}} \quad (3.4)$$

The water content in the solvent is measured and therefore the total water inside the solvent is known, as well as the amount of pure solvent.

$$m_{H_2O,solvent} = w_1 m_{total,1} \quad (3.5)$$

$$m_{solvent} = m_{total,1} (1 - w_1) \quad (3.6)$$

Additional water added to the mixture yields the water amount available before the reaction.

$$m_{H_2O,1} = m_{H_2O,solvent} + m_{H_2O,added} \quad (3.7)$$

The total amount of liquid after the reaction changes, since some water reacts with boron oxide to give boric acid.

$$m_{total,2} = m_{solvent} + m_{H_2O,2} \quad (3.8)$$

The relative water content measured in the Karl-Fischer titrator as given in equation 3.9 can be transformed to give the water mass after the reaction.

$$w_2 = \frac{m_{H_2O,2}}{m_{total,2}} \quad (3.9)$$

$$= \frac{m_{H_2O,2}}{m_{solvent} + m_{H_2O,2}} \quad (3.10)$$

$$m_{H_2O,2} = \frac{w_2 m_{solvent}}{1 - w_2} \quad (3.11)$$

The used up water is the difference between the water content before and after the reaction.

$$m_{H_2O,used} = m_{H_2O,1} - m_{H_2O,2} \quad (3.12)$$

The stoichiometric reacted amount is calculated by the available amount of boron oxide if it is assumed, that water is in excess.

$$m_{H_2O,stoichiometric} = 3 \frac{m_{B_2O_3}}{M_{B_2O_3}} M_{H_2O} \quad (3.13)$$

With these it is possible to calculate the conversion of the observed reaction.

$$x = \frac{m_{H_2O,used}}{m_{H_2O,stoichiometric}} \quad (3.14)$$

### 3.6.2 Total conversion calculations for the formation of borate esters

If an ester is formed the before mentioned equations cannot be used since the amount of 'solvent' does not stay constant. In this case a different approach is necessary.

The total amount of liquid before the reaction is made up of the alcohol and the moisture inside it.

$$m_{total,1} = m_{ROH,1} + m_{H_2O,ROH} \quad (3.15)$$

With the relative amount of water it is possible to evaluate the mass and molar mass of water inside the alcohol.

$$m_{H_2O,ROH} = w_1 m_{total,1} \quad (3.16)$$

$$n_{H_2O,ROH} = \frac{m_{H_2O,1}}{M_{H_2O}} \quad (3.17)$$

Also the alcohol mass and molar mass can be calculated with the relative amount of water.

$$m_{ROH,1} = m_{total,1} (1 - w_1) \quad (3.18)$$

$$n_{ROH,1} = \frac{m_{ROH,1}}{M_{ROH}} \quad (3.19)$$

In a monohydric alcohol occurs reaction 2.23. According to this reaction the moles and masses after the reaction can be calculated the following way, with  $n_r$  describing the reacted moles.

$$n_{ROH,2} = n_{ROH,1} - n_r \quad (3.20)$$

$$m_{ROH,2} = (n_{ROH,1} - n_r) M_{ROH} \quad (3.21)$$

$$n_{Ester,2} = \frac{n_r}{3} \quad (3.22)$$

$$m_{Ester,2} = \frac{n_r}{3} M_{ester} \quad (3.23)$$

$$n_{H_2O,2} = n_{H_2O,1} + n_r \quad (3.24)$$

$$m_{H_2O,2} = (n_{H_2O,1} + n_r) M_{H_2O} \quad (3.25)$$

Since the produced ester is liquid as well, the relative water content has to be calculated by equation 3.26. Transforming this equation gives the reacted moles.

$$w_2 = \frac{n_{H_2O,1} M_{H_2O} + n_r M_{H_2O}}{n_{ROH,1} M_{ROH} - n_r M_{ROH} + \frac{n_r}{3} M_{ester} + n_{H_2O,1} M_{H_2O} + n_r M_{H_2O}} \quad (3.26)$$

$$n_r = \frac{n_{H_2O,1} M_{H_2O} (1 - w_2) - n_{ROH,1} M_{ROH} w_2}{\frac{1}{3} M_{ester} w_2 + M_{H_2O} (w_2 - 1) - M_{ROH} w_2} \quad (3.27)$$

To calculate the conversion the amount of used water and the amount of stoichiometric produced water have to be compared.

$$m_{H_2O,produced} = m_{H_2O,2} - m_{H_2O,ROH} \quad (3.28)$$

$$m_{H_2O,stoichiometric} = \frac{m_{ROH,1}}{M_{ROH}} M_{H_2O} \quad (3.29)$$

Comparing the amount of produced water with the stoichiometric amount gives the conversion for the esterification.

$$x = \frac{m_{H_2O,produced}}{m_{H_2O,stoichiometric}} \quad (3.30)$$

### 3.6.3 Conversion curve calculation

The first step is to define  $t_0 = 0s$  and  $T_{start} = T(t_0)$ . Continuing, the before mentioned heat losses are interpolated for every temperature. These heat losses are summed up to give

$$Q_{loss}(t) = \sum_{t_0}^t [\dot{q}_{loss}(T(t_i))(t_i - t_{i-1})] \quad (3.31)$$

With this value it was possible to calculate the adiabatic temperature curve. Since the experiments were not done under adiabatic conditions, this was necessary to be able to use the formulas described in 2.1.6.

Therefore the molar masses for total conversion were calculated by equations 2.7-2.9 if water was in excess and by equations 2.10-2.12 if boron oxide was in excess.

Additionally, the  $c_p$  values were calculated for the end of the measurement with  $i$  being  $B_2O_3$ ,  $H_3BO_3$ ,  $H_2O$  and solvent.

$$c_{p,i}(t_{end}) = A_i + 10^{-3}B_iT(t_{end}) + 10^5C_iT(t_{end})^{-2} + 10^{-6}D_iT(t_{end})^2 \quad (3.32)$$

$$c_{p,total}(t_{end}) = \sum_{i=0}^{end} (n_i(t_{end})c_{p,i}(t_{end})) \quad (3.33)$$

The adiabatic end temperature can then be calculated by equation 3.34.

$$T_{ad}(t_{end}) = T(t_{end}) + \frac{Q_{loss}(t_{end})}{c_{p,total}(t_{end})} \quad (3.34)$$

With this temperature it is possible to calculate the totally produced heat  $Q_R$  with equation 2.6 and 2.13.

As already described in 2.1.6 the next step is to calculate the conversion as a function of time. Therefore the molar masses of the reactants and the product are calculated by equations 2.14-2.16 if water is in excess and equations 2.17-2.19 if boron oxide is in excess.

Since the real molar masses are known now the real adiabatic temperature can be calculated

$$c_{p,i}(t) = A_i + 10^{-3}B_iT(t) + 10^5C_iT(t)^{-2} + 10^{-6}D_iT(t)^2 \quad (3.35)$$

$$c_{p,total}(t) = \sum_i n_i(t)c_{p,i}(t) \quad (3.36)$$

$$T_{ad}(t) = T(t) + \frac{Q_{loss}(t)}{c_{p,total}(t)} \quad (3.37)$$

With this temperature the enthalpies for each species can be calculated by equation 2.20, the produced heat  $Q(t)$  by 2.21 and the conversion by 2.22.

### 3.6.4 Reactor efficiency

Since the reaction heat of this system changes over the temperature, as described in 2.1.5, it was necessary to assume an average reaction heat that should be produced. This was done by choosing the temperature at  $x=0.5$ . The time at which this occurred is called  $t_{50}$ , as

$x = 0.5$  was achieved until then. The reaction heat was calculated and compared to  $Q_R$  to be able to characterize the efficiency of the reaction.

$$\eta = \frac{Q_R}{\Delta H_R(T(t_{50}))} \quad (3.38)$$



# Chapter 4

## Experiments with different solvents

### 4.1 Triethylene glycol

According to the criteria mentioned in 2.2.5 TEG was selected as the first solvent. It was chosen, since it was readily available, did not pose any danger to health or the environment. Also, since TEG is an alcohol, it was possible to test the influence of the ester formation on the system.

#### 4.1.1 TEG- $\text{H}_3\text{BO}_3$ ratio

Before starting the real experiments it was necessary to do some preliminary tests. First of all it was necessary to evaluate the appropriate reaction vessel. The Karl-Fischer titration (see 3.5.3) showed after the first experiments in an open beaker that air moisture was absorbed into the fluid. This was obvious since the water content after the experiment was higher than before, even though water should have been consumed in the reaction.

After evaluating the appropriate vessel, it was possible to conduct preliminary tests. These tests included mixing triethylene glycol with solids in different mass ratios to figure out the maximal amount of solid so that the mixture is still homogeneous and mixable.

At the beginning of the reaction, a reaction mixture consists of boron oxide, water and solvent. During the course of the reaction, the water reacts with  $\text{B}_2\text{O}_3$  to form  $\text{H}_3\text{BO}_3$ , decreasing the amount of liquid and increasing the amount of solid at the same time. At the end of the reaction, all solid consist of boric acid and the liquid part consists of solvent and possible excess water. To cover the case with the highest solid:liquid ratio, which entails a reaction with  $\lambda = 1$ , boric acid was directly mixed with TEG.

These tests lead to the findings summarized in table 4.1. A video file named `mass_ratio` shows an excerpt of these tests. The goal of this experiment was to find the highest possible ratio, where the mixture is homogeneously mixable. A higher ratio is disadvantageous, because inhomogeneities lead to heat spots and no even temperature distribution. Having more liquid improves the stirrability but also decreases the reachable temperature. Since more material has to be heated, the temperature cannot rise as much as with less solvent. That is the reason, why an optimal ratio has to be found. According to table 4.1 a mass ratio of 1.5g  $\text{H}_3\text{BO}_3$ /1g TEG is this optimal ratio.

Table 4.1: results of the first preliminary tests

g H <sub>3</sub> BO <sub>3</sub> /g TEG	stirrability
2.5:1	too viscose to be able to stir it homogeneously
2:1	partially too viscose to be able to stir it homogeneously
1.5:1	viscose but continuously stirable
1:1	unnecessary low viscosity
0.5:1	unnecessary low viscosity

### 4.1.2 Experiments

The experiments were started and the solid content was calculated so that the added boron oxide forms the amount of boron oxide to give the ratio from the preliminary tests. The parameters changed were the amount of added water, corresponding to the needed water for the reaction of B<sub>2</sub>O<sub>3</sub> to H<sub>3</sub>BO<sub>3</sub>. This factor was called  $\lambda$  with  $\lambda=1$  at stoichiometric conditions. The way  $\lambda$  is calculated can be seen in equation 4.1.

$$\lambda = \frac{n_{H_2O}}{n_{H_2O_{stoich.}}} \quad (4.1)$$

The experiments were scheduled following table 4.2 to cover various influences on the reaction, each 'X' representing one experiment.

Table 4.2: experiment matrix for the experiments with TEG as solvent

	$\lambda=1$	$\lambda=1.5$	$\lambda=3$	$\lambda=5$
B <sub>2</sub> O <sub>3</sub> first	XX	X	XX	X
water first	X	XX	XX	X

## 4.2 Volatile alcohols

As described later on in 5.1.1 TEG reacts with boron oxide to form an ester. To further study this, experiments were conducted with methanol and ethanol. The goal was to study the dependency of the chain length on the reaction. Since the esterification does not need water as a reactant, most of the experiments were conducted without water. A detailed experiment plan can be seen in table 4.3.

Table 4.3: conducted experiments for Methanol and Ethanol

mass relation	Methanol	Ethanol
0.211 g B <sub>2</sub> O <sub>3</sub> /g solvent	X	-
0.422 g B <sub>2</sub> O <sub>3</sub> /g solvent	X	X
0.844 g B <sub>2</sub> O <sub>3</sub> /g solvent	X	XX
1.689 g B <sub>2</sub> O <sub>3</sub> /g solvent	-	X
0.671 g H <sub>3</sub> BO <sub>3</sub> /g solvent	-	X

### 4.3 Various low-boiling non-alcoholic solvents

Since alcoholic solvents were not suited for this application due to their reaction with boron oxide, inert solvents were studied in the next step.

During the previous experiments the reached temperatures did not exceed 100°C. Therefore low-boiling solvents were tested, namely acetone and ethyl acetate. Those two chemicals were chosen since they are commonly used solvents and also belong to two different kinds of solvent classes, namely ketone and ester.

### 4.4 Heptane

To counter the vaporization of the mixture, a higher boiling solvent was chosen again. Since heptane has a boiling point close to the boiling point of water (98.1-98.7 °C) it was chosen to study the reaction in an alkane. For heptane two stirrer speeds were tested as well as different  $\lambda$  and the order in which the educts were added. The experiments done for heptane are summarized in tables 4.4 and 4.5.

Table 4.4: experiments for heptane at 400RPM stirrer speed.

	$\lambda = 1$	$\lambda = 1.5$
B <sub>2</sub> O <sub>3</sub> first	XXXX	XXX
water first	XX	XXX

Table 4.5: experiments for heptane at 800RPM stirrer speed.

	$\lambda = 1$	$\lambda = 1.5$
B <sub>2</sub> O <sub>3</sub> first	X	X
water first	X	X

### 4.5 Methyl isobutyl ketone

Methyl isobutyl ketone was chosen as a representative of ketones. It was selected since it has a fitting boiling point slightly above water (117°C to 118°C). The same experiments as for heptane were conducted, according to table 4.6.

Table 4.6: experiments with MIBK as suspension medium

	$\lambda = 1$	$\lambda = 1.5$
B <sub>2</sub> O <sub>3</sub> first	XXX	XXX
water first	XXX	XXX

## 4.6 Detailed studies of reactions in solvents

### 4.6.1 Drying

In this work only the hydration reaction is studied because the dehydration will be done according to Karel [21]. Since the dehydration process needs a solvent free boric acid it is necessary to remove the solvent from it. In a first step the mixture is filtered in a porcelain Büchner funnel connected to a side-arm flask further connected to a vacuum pump. A filter paper is placed into the funnel. The filtrate contains most of the solvent and excess water. It was disposed of in a container for not-halogenated solvents. The filtered boric acid was dried further in a vacuum drying oven at 40 °C. The drying was tested for three experiments in MIBK.

### 4.6.2 Temperature dependency

To study the influence of temperature on the system, different starting temperatures were chosen. Therefore, the reactor was submerged into a cryostat that was temperature regulated. Also the water added to the reactor was brought to the starting temperature before mixing. At the start of the experiment the reactor was lifted out of the water bath so that the surroundings, ie. surrounding medium and temperature, are the same as for the other experiments. The starting temperatures tested were 2, 10, 40 and 60 °C. All of them were done twice and compared to the standard experiment done at ambient conditions at 25 °C.

### 4.6.3 Various mass relationships

In another test series the influence of the relation between the amount of boron oxide and MIBK was studied. Therefore different ratios varying from the initial ratio of  $0.3475 \frac{\text{gB}_2\text{O}_3}{\text{gMIBK}}$  were studied according to table 4.7. The water amount used was also adapted to keep  $\lambda = 1.5$ .

Table 4.7: changing the relative mass of boron oxide

$\frac{\text{gB}_2\text{O}_3}{\text{gMIBK}}$	$\lambda = 1.5, \text{B}_2\text{O}_3$ first
0.1738	X
0.3041	XX
0.3475	XXX
0.3910	XX
0.4344	X
0.5213	X
0.6951	X

### 4.6.4 Comparison to experiments without solvent

Since another work [20] covered the hydration of boron oxide with liquid water, the results of this work had to be compared with this work's findings. To be able to compare the experiments, a few experiments were performed in the reactor used by Hashemi again with  $\lambda = 1.5$  and adding  $\text{B}_2\text{O}_3$  first.

# Chapter 5

## General results

### 5.1 Triethylene glycol

#### 5.1.1 Experiments

With the evaluated solid:liquid ratio it was possible to start the experiments. The first step was to either add water or  $B_2O_3$  to the solvent. The temperatures measured for these cases are seen in figure 5.1 and 5.2, respectively. When the water is added a sudden temperature increase occurs. This increase is due to the mixing enthalpy that is released when water and TEG are mixed. This corresponds to the negative mixing enthalpy seen in figure 2.5.

When just  $B_2O_3$  is added the temperature increases over time. This increase can not be correlated to a mixing enthalpy but only a reaction.

Since only the water amount is changed and the  $B_2O_3$  is kept constant, all the experiments where boron oxide is added first should be the same. Figure 5.2 shows this trend. The curves all exhibit the same trend with the same temperature increase, and a similar reaction time. When adding the second reagent, the temperature increases more if  $\lambda$  is kept low. This is due to the fact, that less excess water is present, reducing the amount of material that has to be heated and therefore reducing the systems total heat capacity. When comparing two experiments with the same  $\lambda$  it is visible, that the temperature increase is higher, if  $B_2O_3$  is added to the water-TEG mixture. This corresponds to figures 5.1 and 5.2, where the temperature increase is also higher, when  $B_2O_3$  is added to TEG. Therefore it can be assumed, that some of the boron oxide reacts with the alcohol before being hydrolysed by water.

#### 5.1.2 Conversion calculations

Table 5.1 shows an excerpt of the results for the Karl-Fischer titration in TEG. Since not only boron oxide but also water was added to TEG, it was assumed that no ester remained and that by hydrolysing the ester the desired boric acid was produced. The values were calculated according to equations 3.3-3.14.

This table shows the average conversion for every experiment at a certain  $\lambda$ . The separate conversions can be taken from table 2 in the appendix. The values show, that for a stoichiometric mixture, a relatively high conversion around 0.8 is achievable. If a higher  $\lambda$  is chosen, the calculated conversions exceed 1. This is due to the fact, that the water content in TEG is rather high, with about 20 weight% at  $\lambda = 1.5$ . Since the Karl-Fischer titrator is designed to measure small water contents in the range of ppm to a few weight%, the result

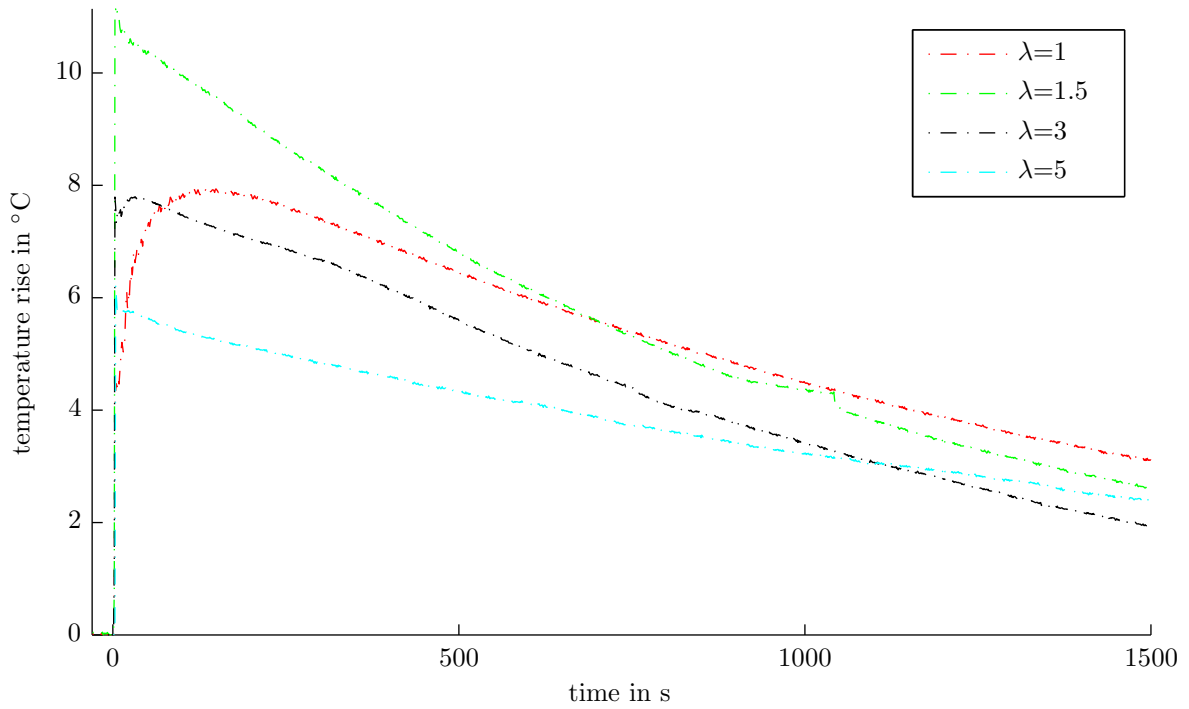
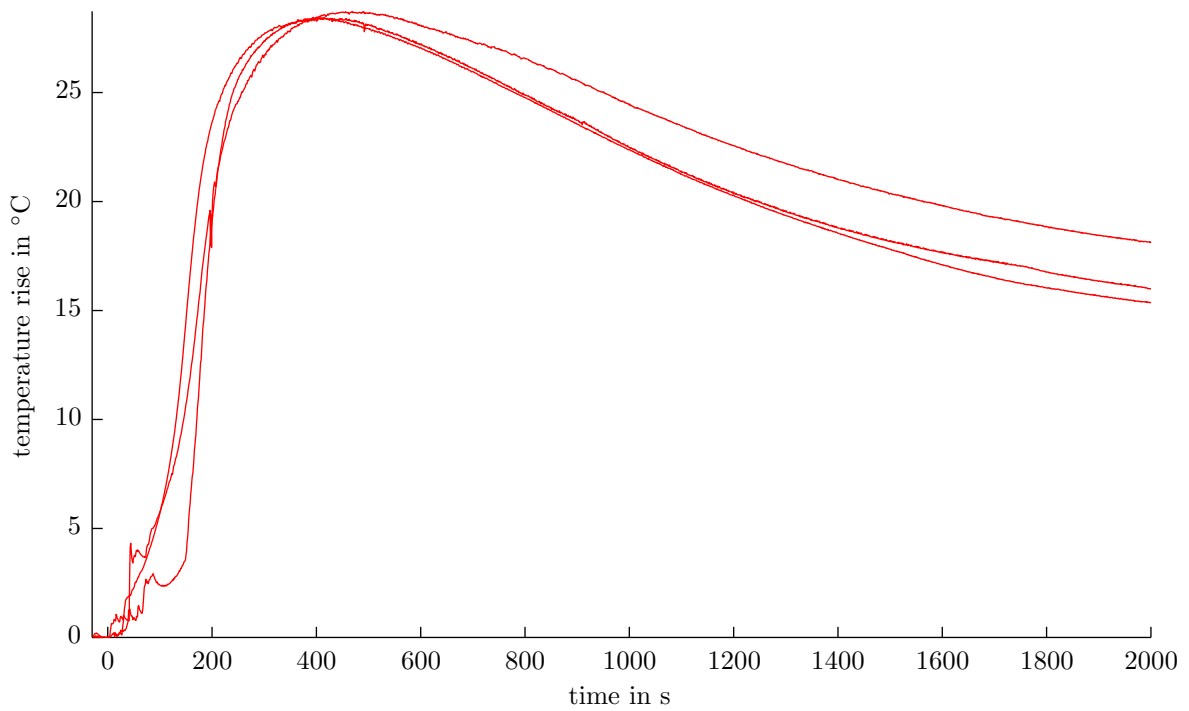


Figure 5.1: dependency of the temperature when water is added to TEG

Figure 5.2: Temperature change when  $B_2O_3$  is added to TEG

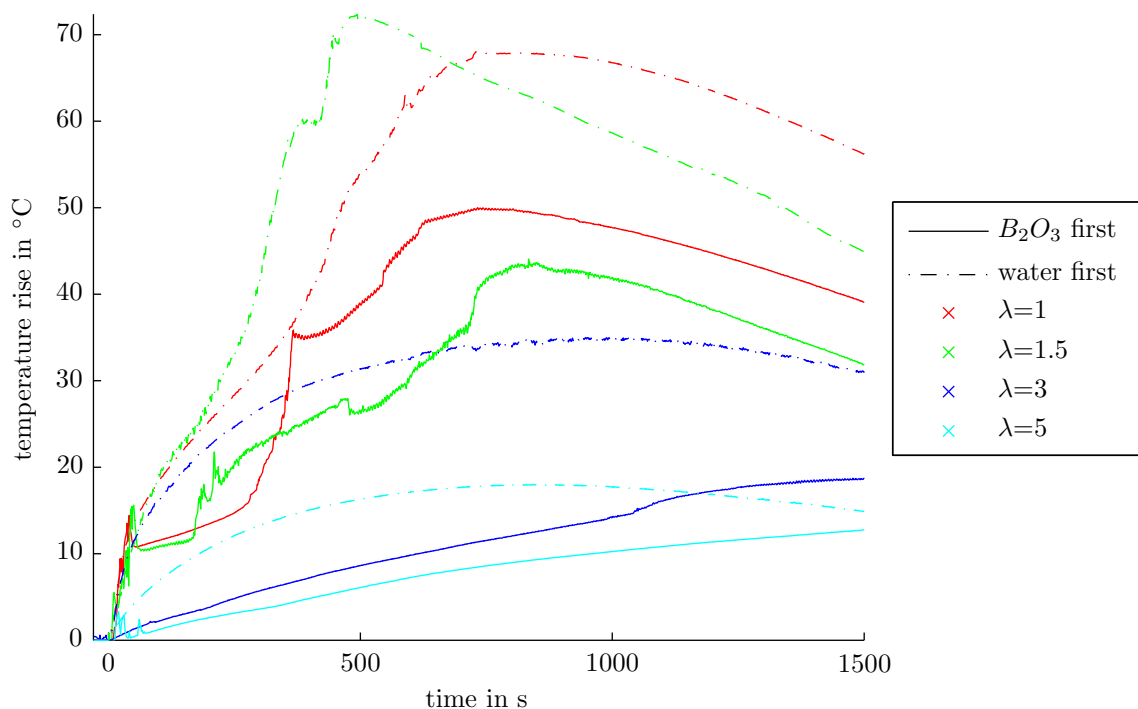


Figure 5.3: Depicts the temperature for various cases when the second reagent is added to TEG.

is inexact, if a high water content is measured. One reason for this inaccuracy is that the measured sample size has to be small, to be able to measure high water contents with this titrator, therefore decreasing the accuracy of the titrator.

Table 5.1: Excerpt of the conversion calculations when assuming that the hydrolysed product is boric acid. The experiment parameters are taken from table 4.2. The rest of the calculations can be found in table 2.

experiment	$\lambda = 1$	$\lambda = 1.5$	$\lambda = 3$	$\lambda = 5$
conversion x	0.79	1.14	2.31	3.89

## 5.2 Low-boiling solvents

### 5.2.1 Low-boiling alcohols

To further study the reaction between alcohols and boron oxide, the reaction was carried out with methanol and ethanol. Figure 5.4 depicts the temperature increase when  $B_2O_3$  is added to the corresponding alcohol. As assumed, for different amounts of boron oxide in the alcohol the maximal reachable temperature changes. The more  $B_2O_3$  was added the more could react and the more heat could be produced, leading to a higher temperature. Another observation is that the reaction occurs slower with less material, especially visible for methanol. It can also be seen, that the maximal reached temperature is above the boiling

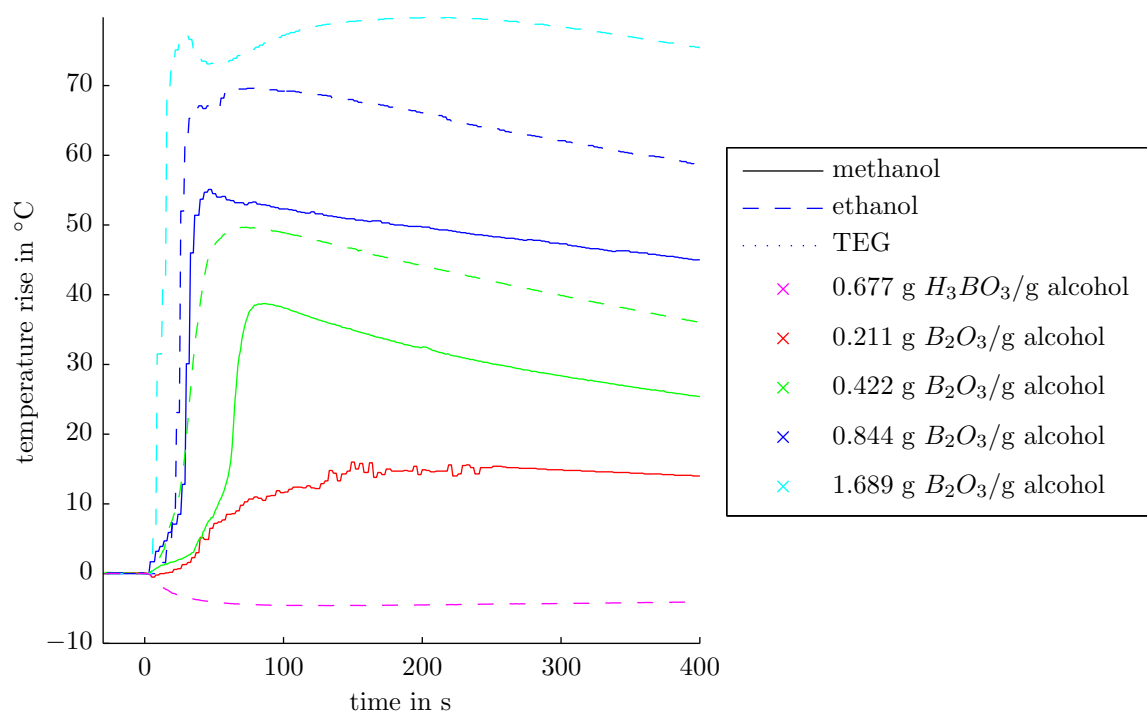


Figure 5.4: Temperature change over time when B<sub>2</sub>O<sub>3</sub> or H<sub>3</sub>BO<sub>3</sub> is added to different alcohols

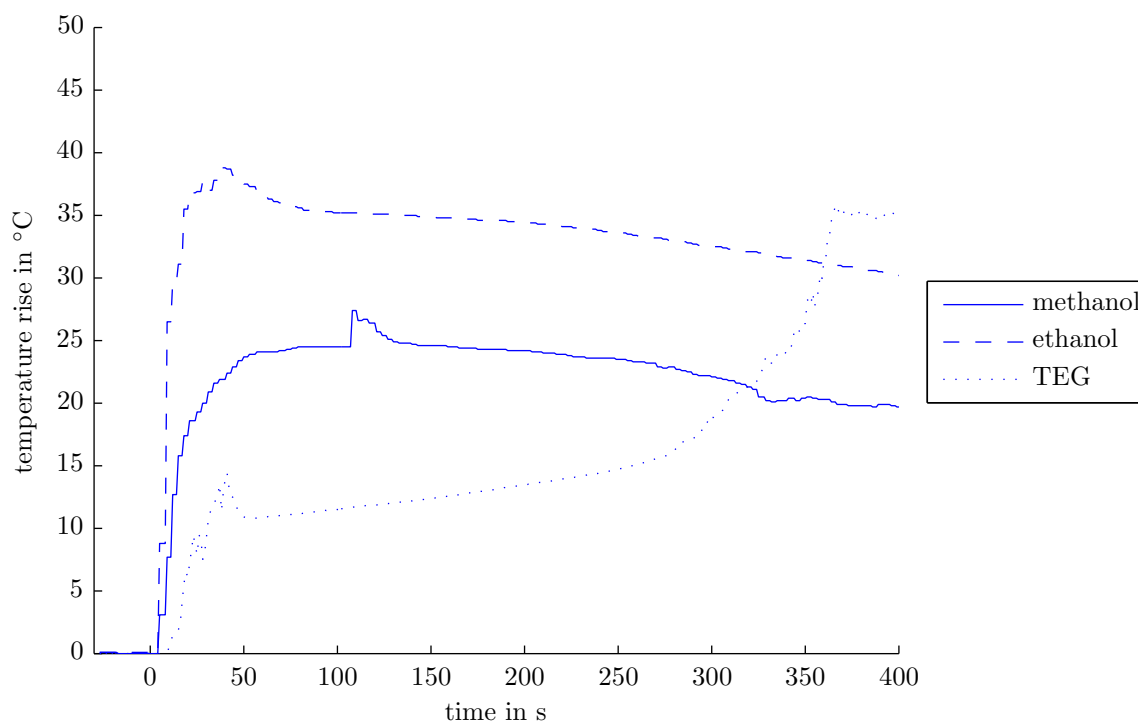


Figure 5.5: Temperature dependency over time when water is added to a B<sub>2</sub>O<sub>3</sub>/alcohol mixture with a ratio of 0.844 g B<sub>2</sub>O<sub>3</sub>/g alcohol.



points, 64.7 °C for methanol and 78.37 °C for ethanol, of the used solvents. This observations are according to figures 2.6a and 2.7a, since a mixture of water and the alcohols has a higher boiling point, than the pure alcohol.

Additionally, the previous measurements for TEG were also added in the plot. It shows, that the reaction occurs slower for TEG than for the other two alcohols. This might be related to the higher viscosity of TEG.

For methanol and the produced trimethyl borate the resulting temperature is also higher than the boiling point of the ester, which is between 68 and 69 °C. In the case of ethanol the boiling point of the ester triethyl borate is not reached since this boiling point is 118 °C. Figure 5.4 also shows what happens if boric acid is added to ethanol. The esterification with  $\text{H}_3\text{BO}_3$  is an endothermal process and follows equation 2.23.

In figure 5.5 the temperature curve for adding water to the alcohol- $\text{B}_2\text{O}_3$ -mixture is visible. According to Steinberg et. al [38] hydrolysis, following equation 2.28, takes place when water is added to a boron ester. This hydrolysis is occurring fast, which can be seen in the fast temperature increase. A different curve is visible for TEG, where the hydrolysis takes a longer time. This might again be correlating with the higher viscosity of the mixture.

In one case the water concentration after the reaction between methanol and  $\text{B}_2\text{O}_3$  was measured with Karl-Fischer titration and can be seen in table 1 in the appendix. The concentration before the reaction was 0 weight% since the methanol was purified beforehand and the water concentration after the reaction was measured as 16 weight% water. The obtained values cannot be used for further analysis since for the experiments with boron oxide it is not possible to measure if and how much the reaction 2.26 occurs. Only the reaction 2.27 could be accounted for with these measurements.

For the reaction of ethanol and boric acid a Karl-Fischer titration was conducted as well. Table 1 in the appendix shows the results for these measurements. The calculated conversion of 16.7 weight% water has to be increased if this system should be used as a thermochemical energy storage.

Still, these systems were studied for their possibility as a thermochemical energy storage due to the observed heat release. Comparing table 2.7 and figure 2.1 shows that the energy produced is higher for the system  $\text{B}_2\text{O}_3/\text{H}_3\text{BO}_3$  than for the two studied esters.

Also, it is hard to produce pure esters and even if they are purified, their low hydrolytic stability, make a long lasting storage difficult.

Following all the mentioned difficulties and disadvantages, boron esters were not added as candidates for TCES.

## 5.2.2 Low-boiling non-alcohols

To study the reaction in a solvent in more detail, other organic compounds were used. In a first step readily available low-boiling solvents were chosen. These solvents are acetone and ethyl acetate, respectively. Figure 5.6 depicts the measured curves when only one of the reagents is added. As already mentioned before, when only water is added to the mixture, an immediate temperature change is observable. For acetone this temperature change is positive, in the case of ethyl acetate it is negative. This corresponds with the observations from figures 2.8a and 2.10a. When just  $\text{B}_2\text{O}_3$  is added, a slight temperature increase over time is observable. This might be due to the small amount of water in the solvents. Table 3 shows that ethyl acetate has around 730 ppm of water that could react as seen in figure

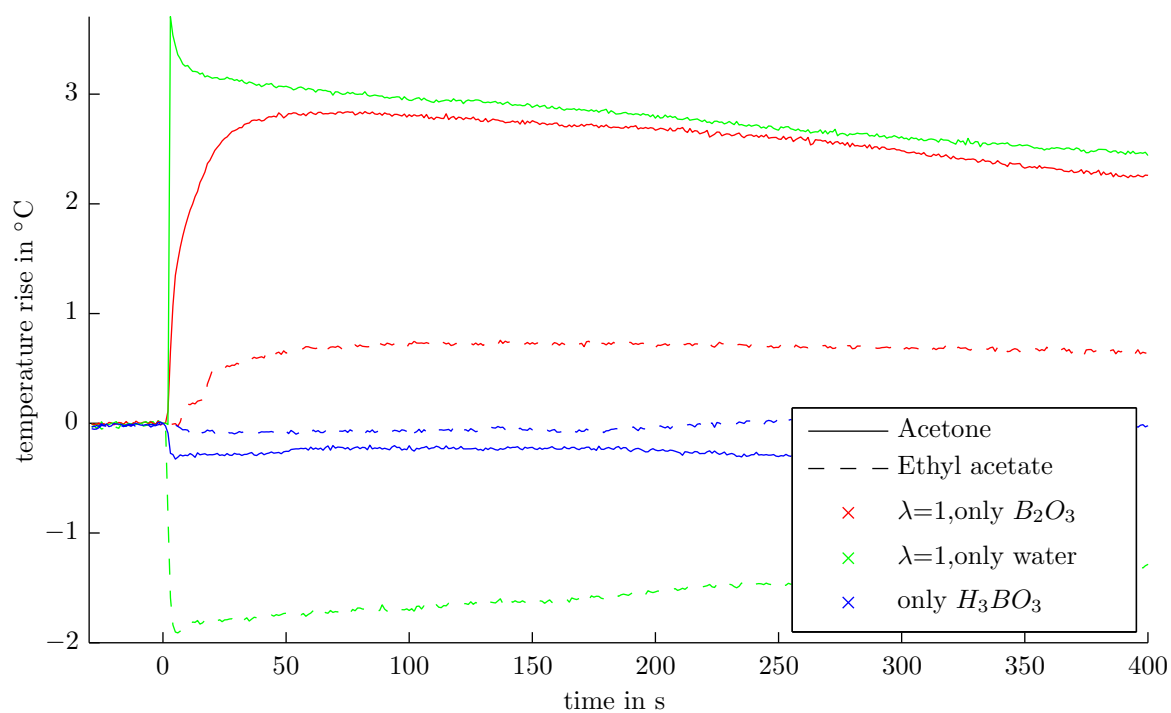


Figure 5.6: Compares the cases of adding  $B_2O_3$  or water to acetone and ethyl acetate. Furthermore the case of adding  $H_3BO_3$  is depicted.

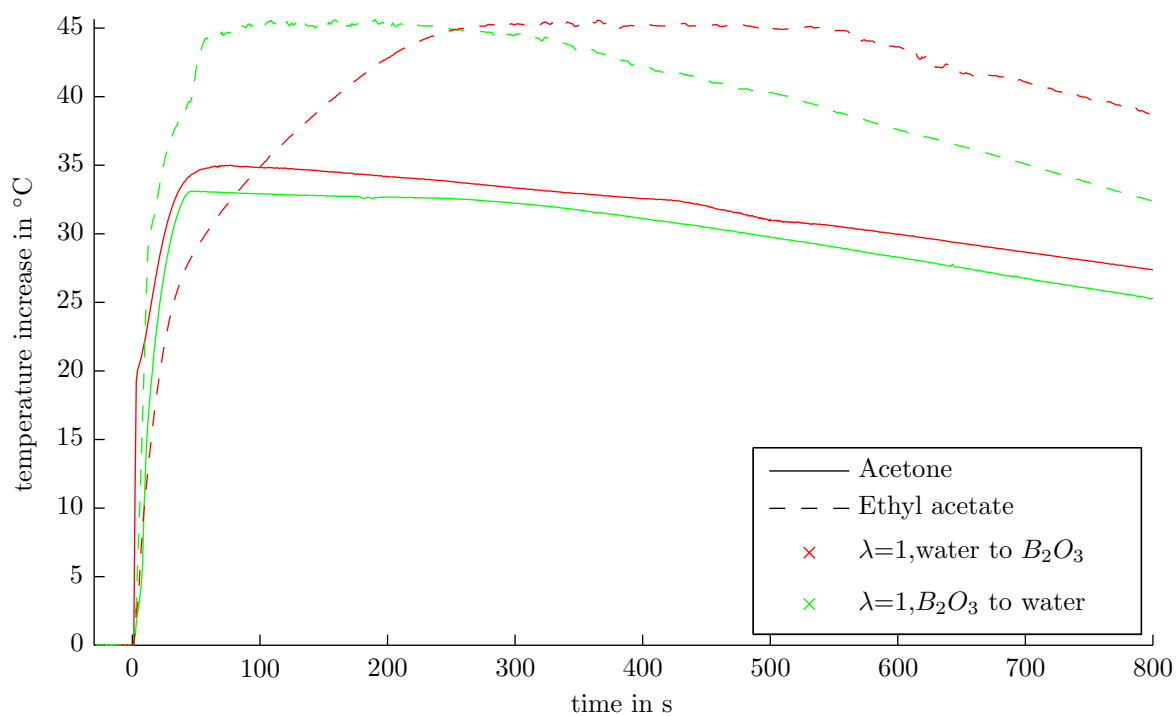


Figure 5.7: Shows the differences between adding water to  $B_2O_3$  and  $B_2O_3$  to water in acetone and ethyl acetate.

5.6. The conversion calculated for the reaction with  $\lambda = 1$  is about 0.9 when referring to the reacted boron oxide.

The corresponding temperature curve to the reaction mentioned in table 3 can be found in figure 5.7. This figure shows the processes of adding the second reagent. Furthermore, the curve for the product, boric acid, is added as comparison. It can be seen that the product does not react with the solvent, therefore all observed temperature changes are due to reactions between water and boron oxide, apart from the mixing enthalpies seen in figure 5.6.

For acetone the order of adding the reagents does not influence the maximal reachable temperature. This is due to the fact, that the boiling temperature of the mixture is reached and some of the mixture evaporates, holding the temperature constant. The difference is that the temperature increases faster, when water is added to  $B_2O_3$ , probably due to the mixing enthalpy between acetone and water, see figure 5.6, lifting the temperature immediately.

If the reaction is conducted in ethyl acetate the order of adding the reactants has an influence. If  $B_2O_3$  is added to the water/ethyl acetate mixture the reaction occurs faster than the other way around, even though the maximal reached temperature is still the same, again with some of the mixture evaporating.

## 5.3 Heptane

In the following the results for Heptane are shown. Figure 5.8 depicts all measurements at 400RPM, which was chosen as the lower tested stirrer speed. It shows that the reaction is faster if  $\lambda = 1$  is applied. This tendency can also be seen in 5.9 and 5.10, where only the reactions with adding  $B_2O_3$  or water first are compared.

Figure 5.8 also shows that the reactions occur faster if water is added before  $B_2O_3$ , which can be seen more clearly in 5.11. Here the cases for adding water or  $B_2O_3$  first are compared for  $\lambda=1.5$ .

Figures 5.9-5.11 also show the measurements for 800RPM. These experiments follow all the trends mentioned above. Additionally the reaction is faster in these cases compared to their counterparts with 400RPM.

The Karl-Fischer titration conducted according to 3.5.3 lead to unexpected values, which can be seen in the appendix in table 4. They show a conversion of nearly 1, if  $\lambda = 1$  is used but a conversion of 1.5, if  $\lambda = 1.5$  is studied. This is due to the fact that even when an excess of water should remain in the solvent, the measured water content is still only in the range of ppm. This might be due to the fact that water and heptane are nearly immiscible, as shown in figure 2.11, and therefore the sample taken is not representing the real concentrations. Furthermore, if the samples were stored over night, nearly all the liquid inside the microtubes vanished. The heptane inside probably diffused through the plastic. To counter this problem, the samples were measured directly after taking them.

The experiments with heptane also exhibited some other challenges. When adding the second reaction partner the solids sank to the bottom of the reaction flask. This behaviour is depicted in the video file separation. This file not only shows the start of the reaction and the following separation, but also how the liquid and solid are mixing again at later times of the reaction. Due to this behaviour it was difficult to get reproducible data which can be clearly seen in 5.8-5.10. That is the reason for only one measurement with 800RPM for every case.

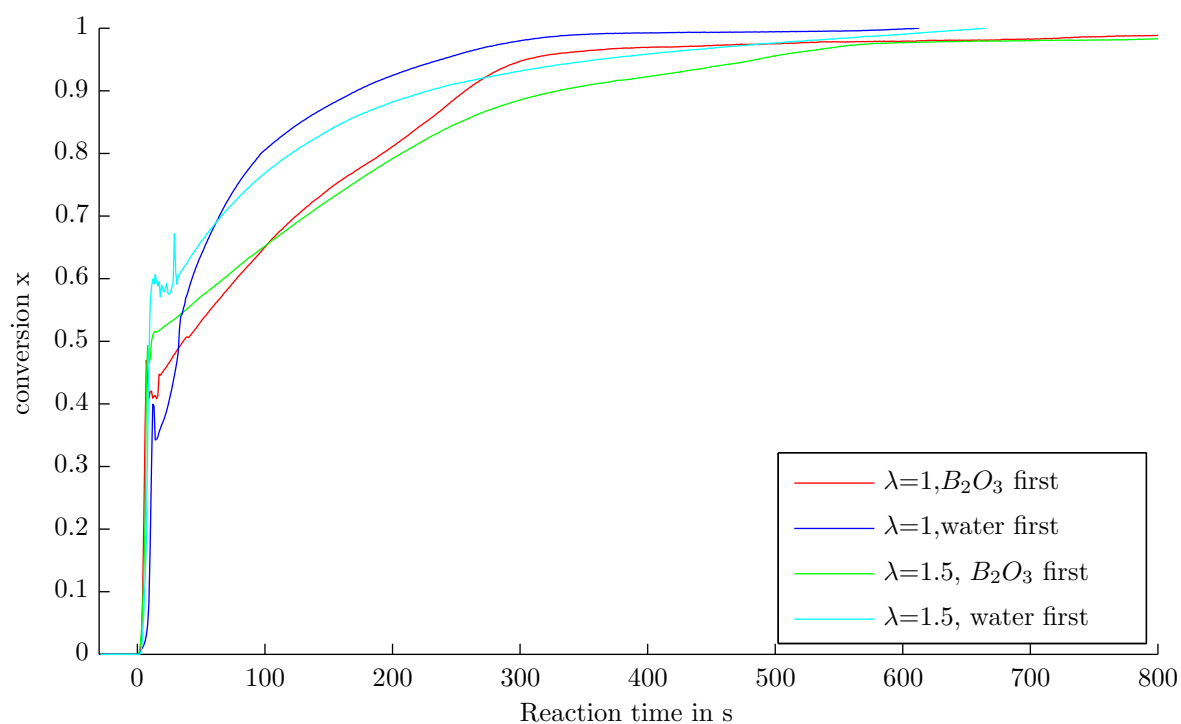


Figure 5.8: Comparison between all experiments done with Heptane at 400RPM.

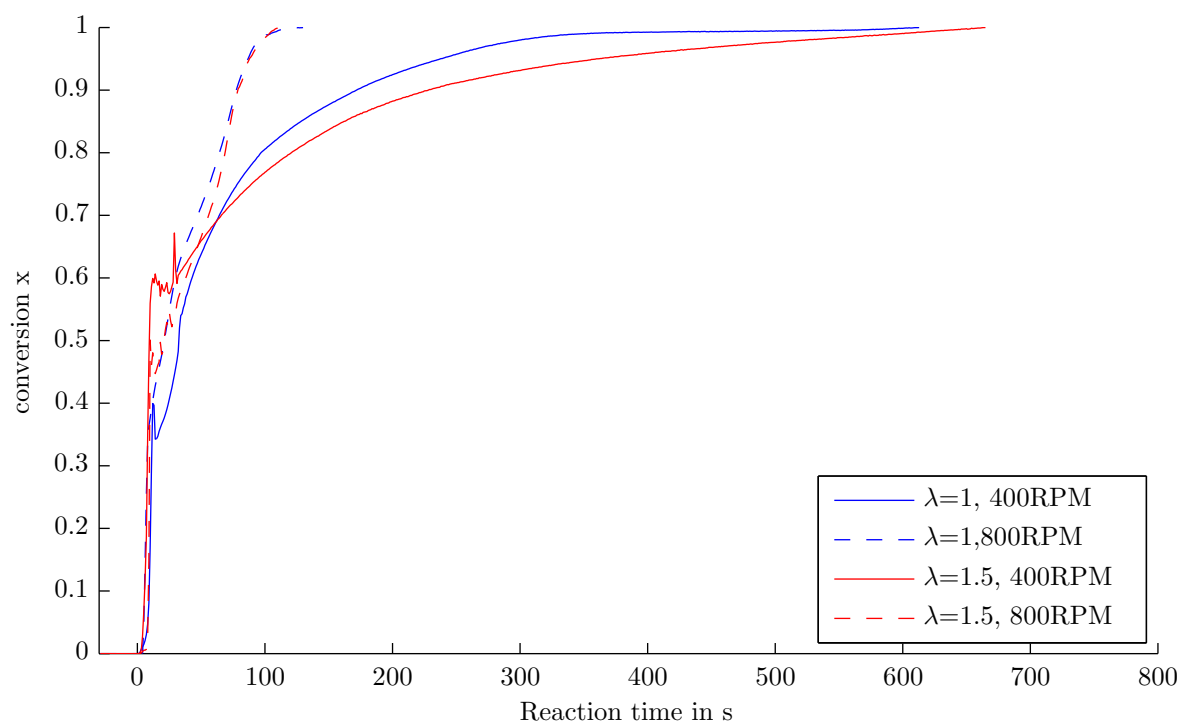


Figure 5.9: Compares the reactions when boron oxide was added to a heptane-water mixture done for different  $\lambda$  and rotor speeds

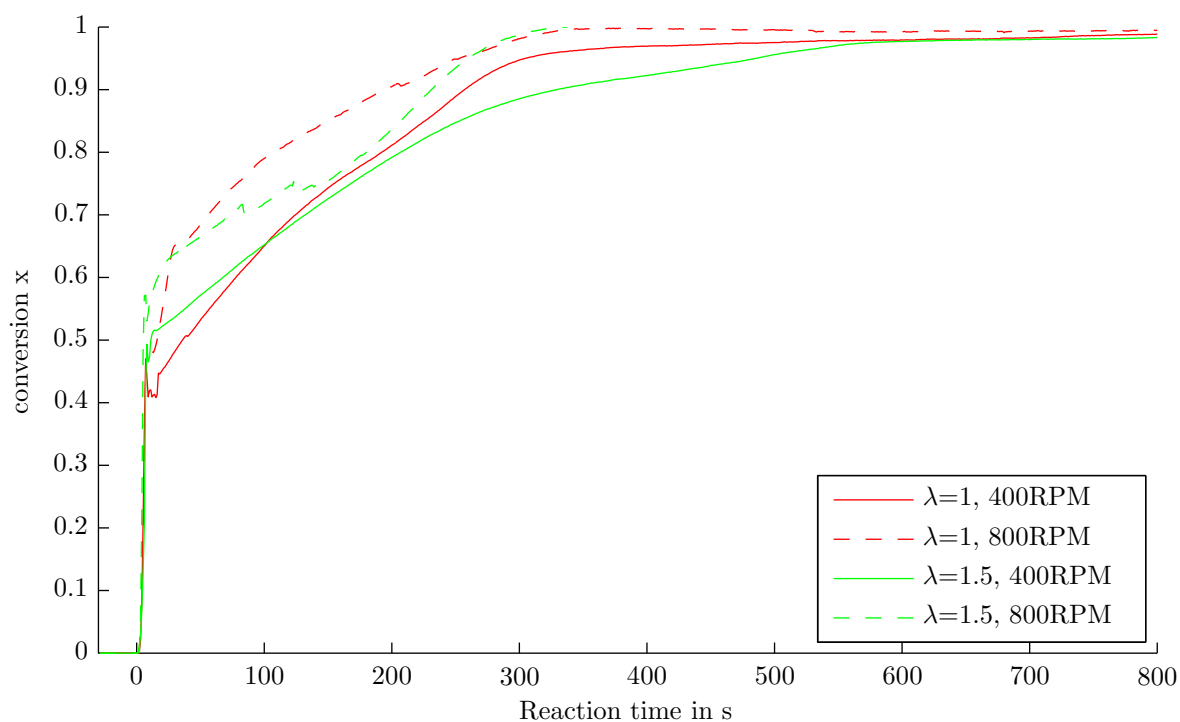


Figure 5.10: Shows experiments, where water was added to a heptane- $B_2O_3$  mixture, done for different  $\lambda$  and rotor speeds.

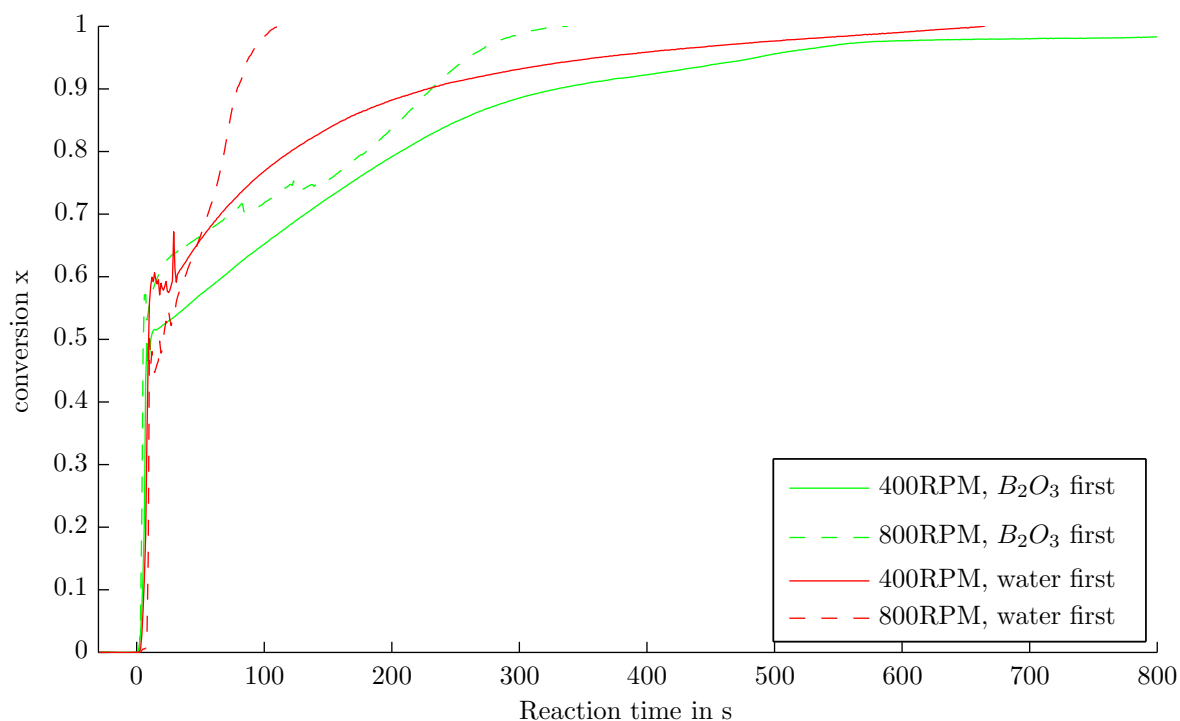


Figure 5.11: Compares experiments, where water was added to a  $B_2O_3$ -heptane mixture and where  $B_2O_3$  was added to a water-heptane mixture.  $\lambda=1.5$  was kept constant and different rotor speeds are observed.

## 5.4 Methyl isobutyl ketone

The experiments done according to table 4.6 lead to figure 5.12. This figure shows that the reaction goes faster if  $B_2O_3$  is added before the water, which can be seen in more detail in figure 5.13. Figure 5.12 also shows that  $\lambda$  does not have a measurable influence on the reaction. The figures 5.14 and 5.15 also show that  $\lambda$  does not have an influence.

To further study the reproducibility of the experiment,  $t_{50}$  and the efficiency were compared. Figure 5.16 (a) shows that there is a statistically relevant difference for  $t_{50}$  depending on the order of adding the reaction partners. This corresponds to figure 5.12, where the reaction occurs faster when  $B_2O_3$  is added first. The efficiency, on the other hand, does not exhibit a trend regarding the feeding order. Only if the order and the water content are changed, a different efficiency was observed. In this case, a slower reaction corresponds with a better efficiency regarding the heat output.

## 5.5 Evaluating the best solvent

To be able to choose the solvent for further studies, several aspects had to be checked. One aspect is that no reaction between solvent and any reaction partners should occur, therefore excluding all alcohols studied. Furthermore, since the conversion is calculated by the released heat and therefore the temperature, no evaporation should occur, since this distorts the results calculated. Following this approach only heptane and MIBK are possible candidates for a detailed study.

### 5.5.1 Comparing heptane and MIBK

Figure 5.17 shows the conversion for various experiments in MIBK and heptane. The initial reaction occurs faster in heptane, which can be seen in more detail in figure 5.18. At the start of the reaction, the conversion increases more in heptane but after the initial fast reaction rate, the rate is about the same in heptane and MIBK.

A further analysis of the experiments showed that the efficiency of the two systems is the same, but  $t_{50}$  is a lot higher in MIBK compared to heptane. This trend can be seen in figure 5.19. Assuming Gaussian distribution with different standard deviations lead to a p-value of 0.0080. The criterion that the p-value has to be below 0.05 for significantly different average values allows to say that  $t_{50}$  is statistically different for the two cases. Two significantly different values are marked by a \*.

Figure 5.20 shows the temperature rise during the reaction in heptane and MIBK. This figure shows, that the temperature rises higher, if the reaction is performed in MIBK.

But even though the reaction occurs faster in heptane, MIBK was chosen for a further investigation since it was not possible to produce reproducible data in heptane. This might be due to the separation of liquid and solid at the start of the reaction. Another criteria was the higher reachable temperature in MIBK compared to heptane.

The case  $\lambda=1.5$  and  $B_2O_3$  first was chosen as the base line for additional experiments. This case was chosen, since the reaction occurred faster if boron oxide was added to MIBK before the water.  $\lambda = 1.5$  was chosen to counter weighting inaccuracies. Since  $\lambda = 1$  equals stoichiometric conditions, already small changes in weight can lead to either water or boron oxide being in excess. To be sure that always water is in excess,  $\lambda = 1.5$  was selected, so that it is not necessary to consider this problem.

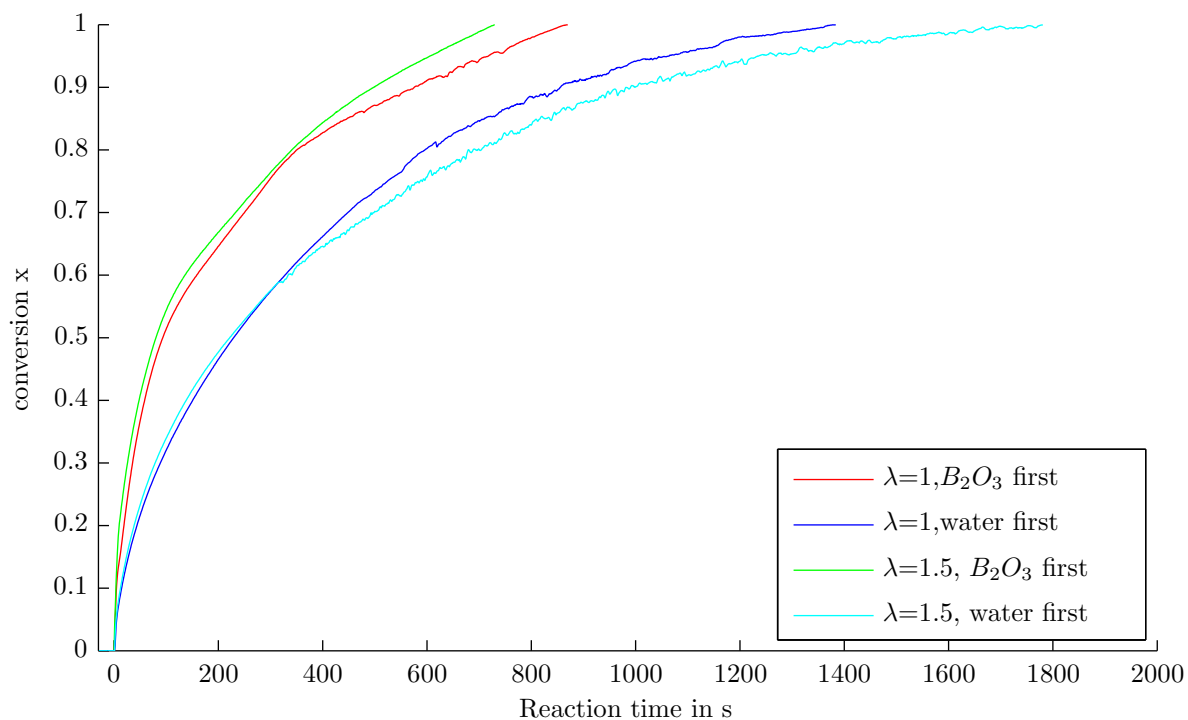
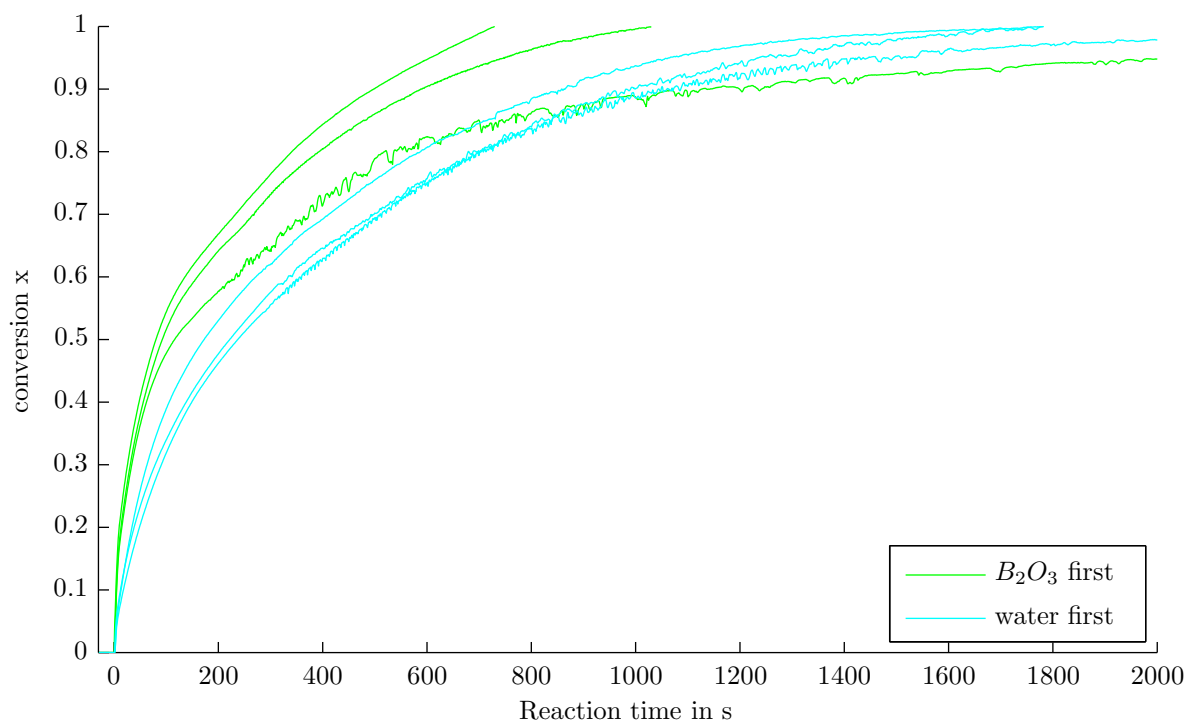


Figure 5.12: Comparison between all experiments done with MIBK

Figure 5.13: Compares adding water or  $B_2O_3$  first into MIBK for  $\lambda=1.5$

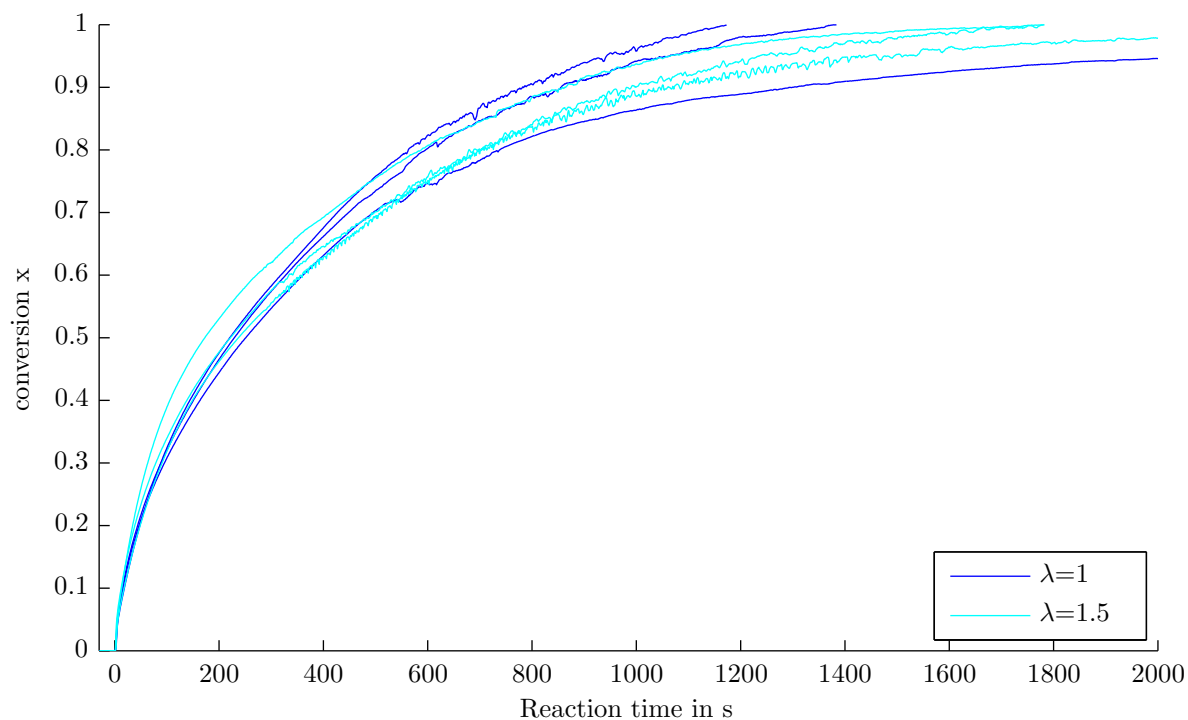


Figure 5.14: Compares the cases of adding water first into MIBK with different  $\lambda$

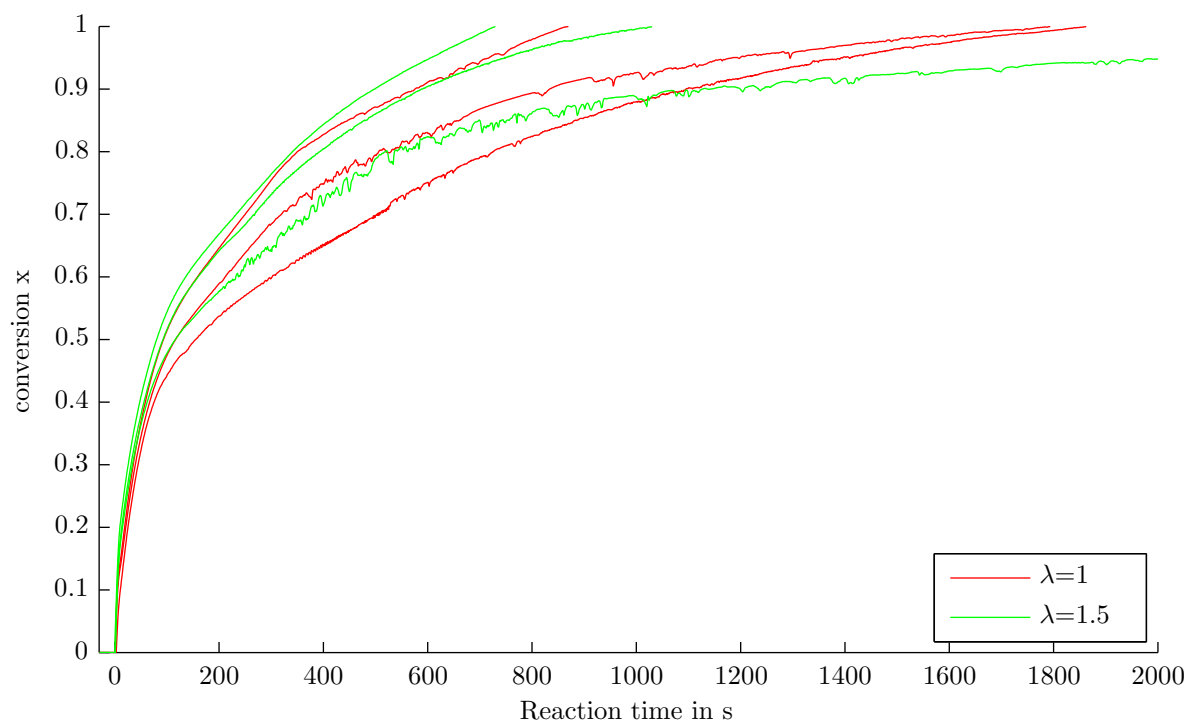


Figure 5.15: Shows the differences for the cases of adding  $B_2O_3$  depending on  $\lambda$  into MIBK



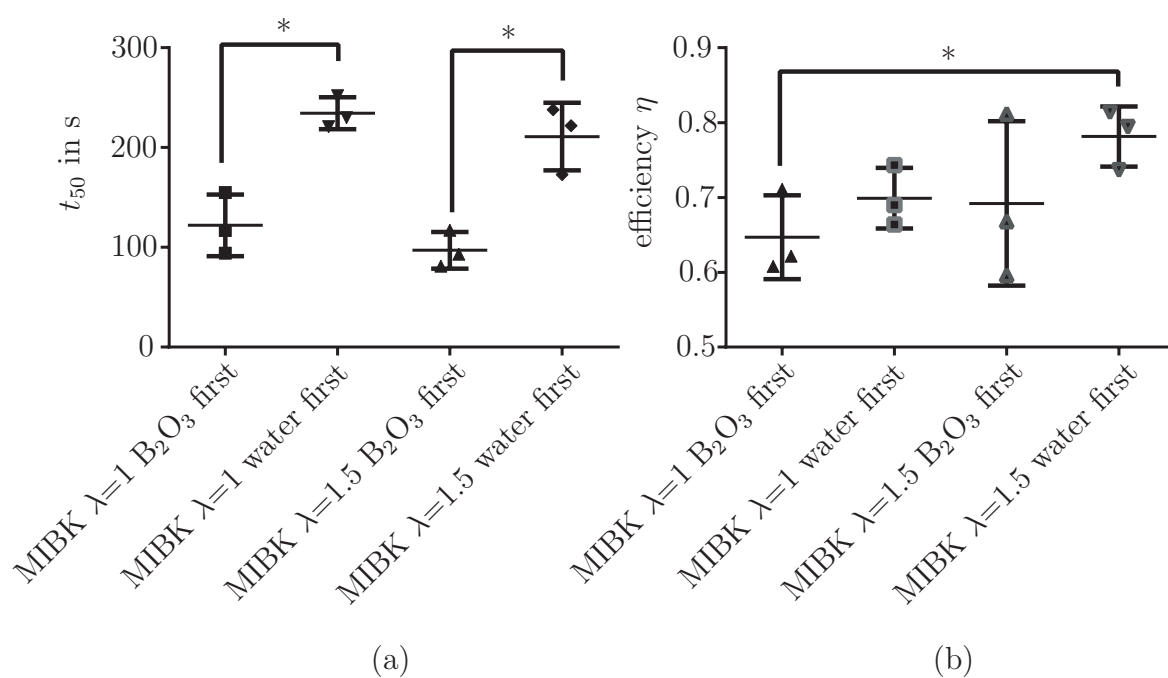


Figure 5.16: The graphs show the experiments in MIBK. It depicts the average value and the standard deviation. (a) shows  $t_{50}$  and (b) the efficiency of the system.

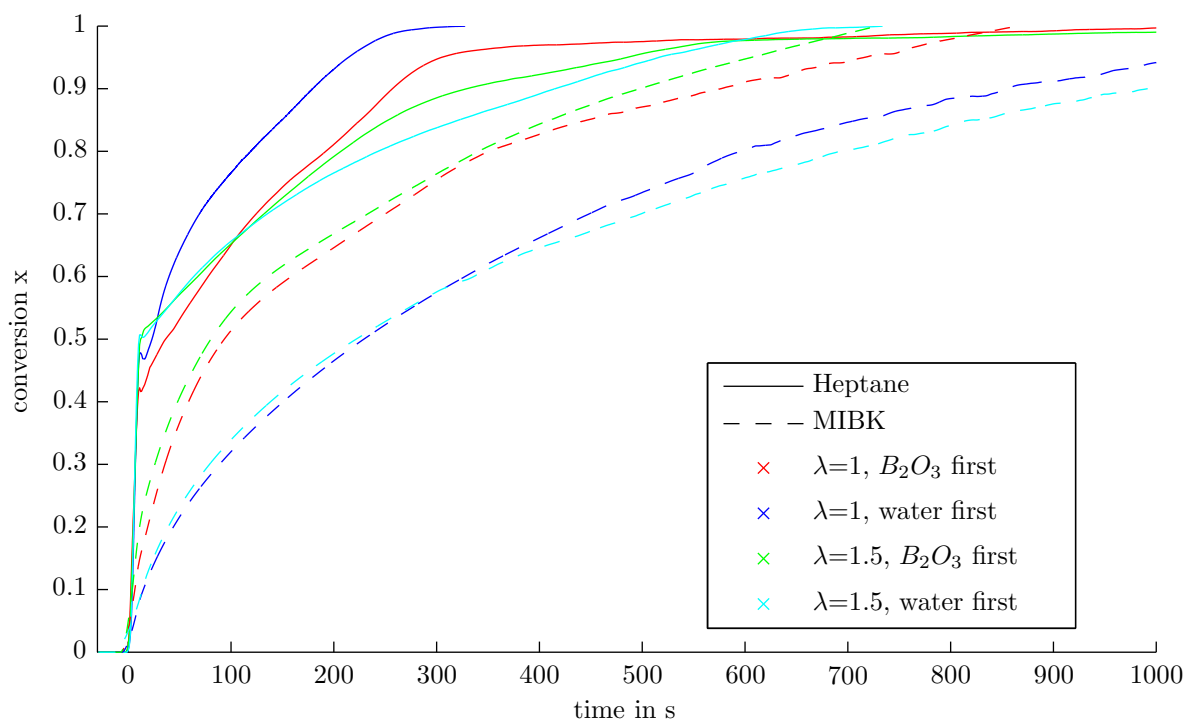


Figure 5.17: Compares the conversion in heptane and MIBK

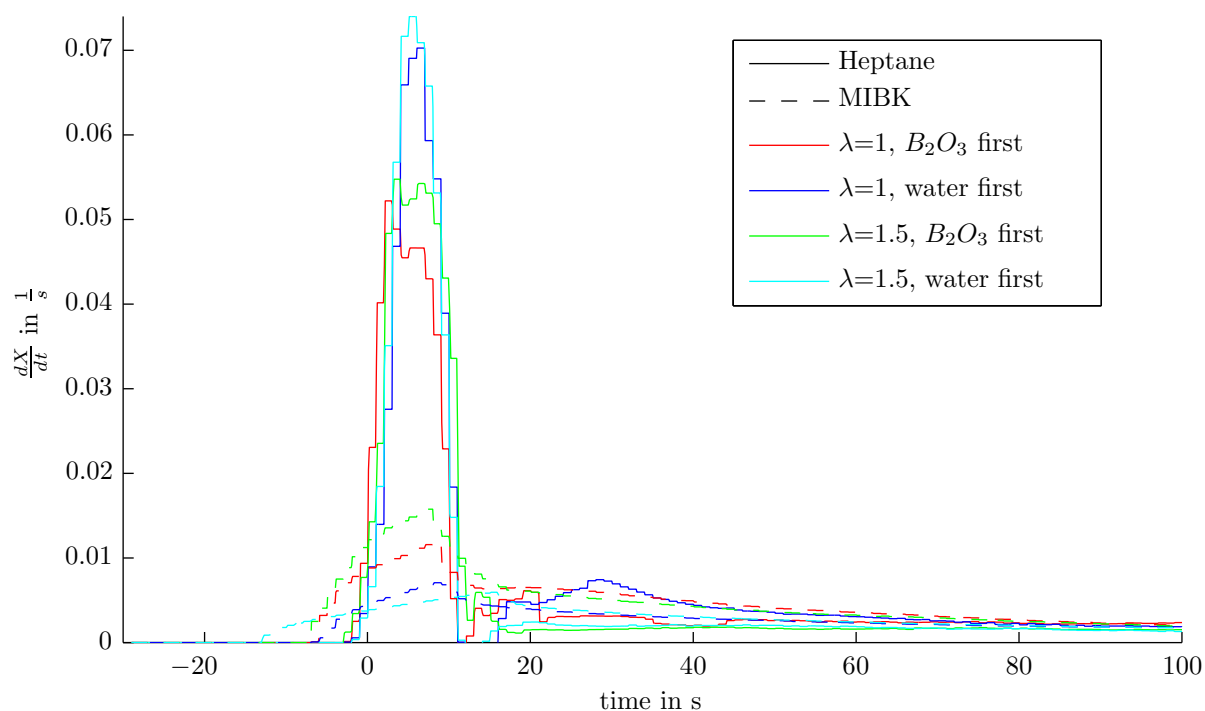


Figure 5.18: Shows the different conversion rates in heptane and MIBK

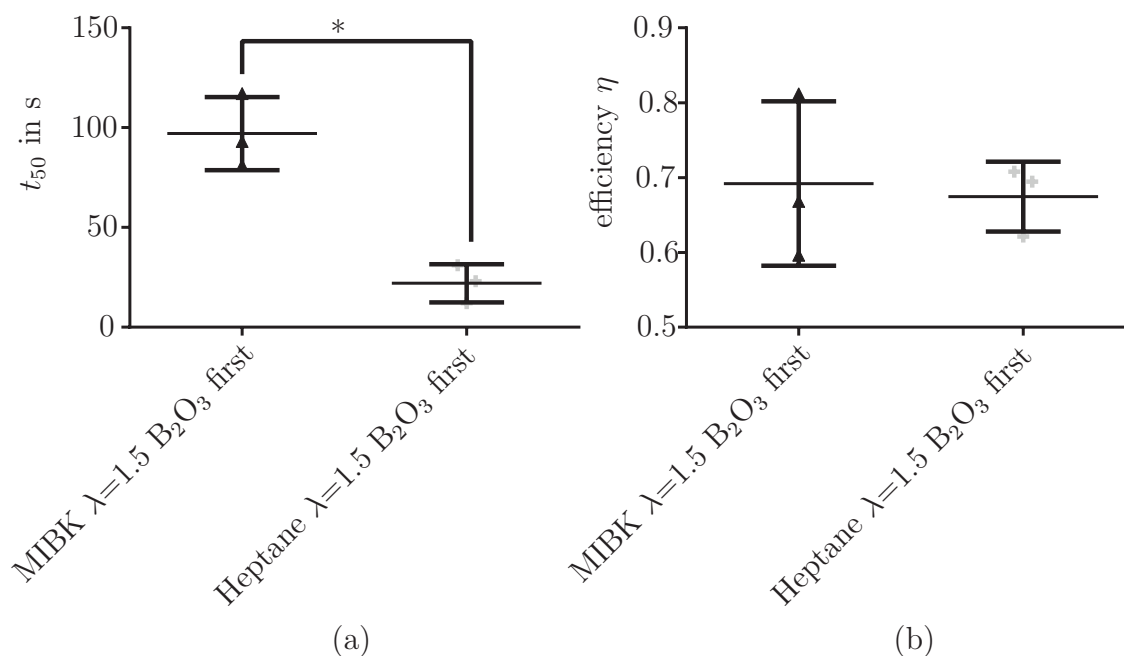


Figure 5.19: The graphs show the experiments with  $\lambda=1.5$  and  $B_2O_3$  first in MIBK and heptane. It depicts the average value and the standard deviation. (a) shows  $t_{50}$  and (b) the efficiency of the system.

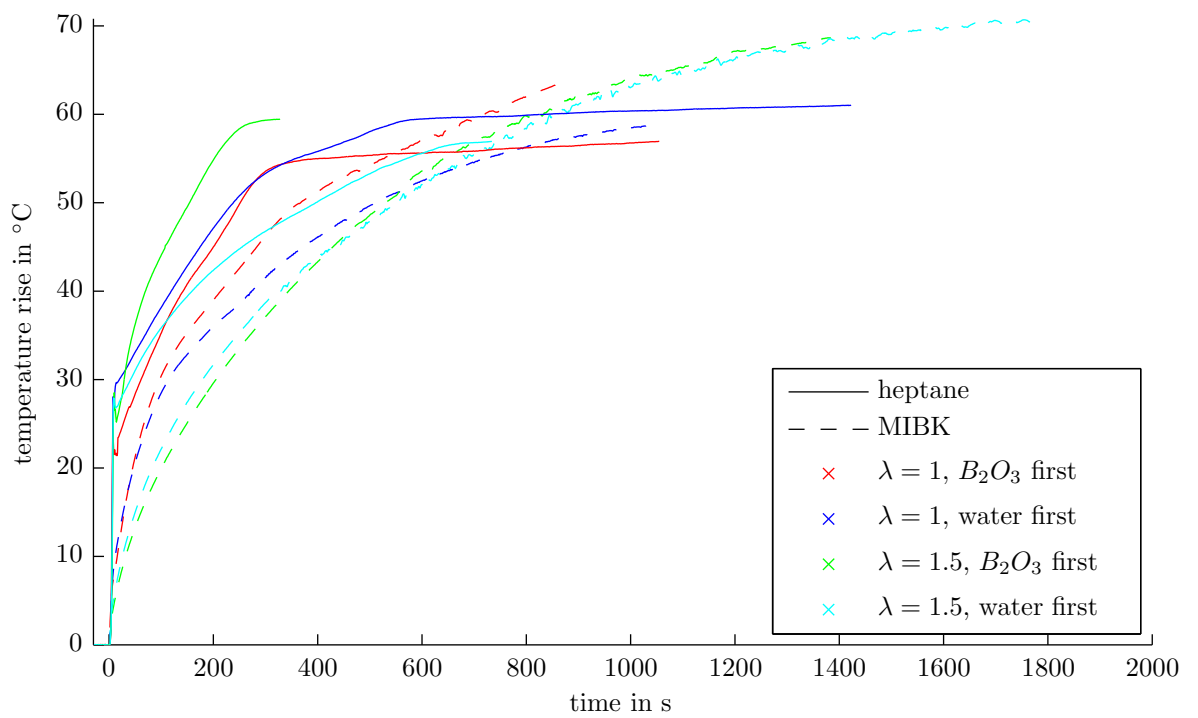


Figure 5.20: Temperature rise for different reactions in heptane and MIBK.



# Chapter 6

## Detailed investigations in MIBK

### 6.0.2 Drying

Since boric acid decomposes to boron oxide and water at higher temperatures [52] the drying could not be done in a regular drying oven. To be able to dry  $\text{H}_3\text{BO}_3$  at low temperatures, it is necessary to apply a vacuum as well. The results of the drying experiments are summarized in the appendix in table 5. Comparing the liquid mass that should be in the reactor, with the liquid mass in the Büchner flask after titrating, a big discrepancy is visible. This might be due to the vacuum pump decreasing the pressure too much so that the liquid partly evaporated in the flask.

The filtration was performed with a fraction of the material and it was assumed that this fraction had the average composition of the mixture. With this it was possible to calculate the expected solid amount after the filtration. The obtained dried solid amount is approximately the same as the expected amount. Therefore it is possible to say, that the vacuum drying oven worked sufficiently to remove the solvent from the boric acid.

### 6.1 NMR spectroscopy

One way to measure, if all of the boron oxide reacted was to study the filtrate in a  $^{11}\text{B}$ -NMR. With these NMRs it is possible to depict the chemical surroundings of a bor atom in a molecule. Since the peaks in figure 6.2 and figure 6.3 are at the same position, the bor atoms in both molecules have the same adjacent molecules. Since one of the samples was boric acid, it is possible to assume that this peak marks boric acid. Therefore it is possible to assume that at least in the filtrate no educt can be found anymore.

To compare the NMRs of  $\text{H}_3\text{BO}_3$  and  $\text{B}_2\text{O}_3$ , boron oxide was mixed with MIBK and filtered afterwards. The NMR for this sample can be seen in figure 6.4. This figure shows no bor peaks, so it is possible to assume, that boron oxide is not soluble in MIBK.

### 6.2 XRD

One dried product was also studied in an XRD to evaluate if the obtained product consists of  $\text{H}_3\text{BO}_3$  only. Figure 6.5 shows the XRD measured for the product and figure 6.6 proves that only boric acid and no boron oxide forms the crystals. Therefore it was proven that the product only consists of  $\text{H}_3\text{BO}_3$  and a total conversion is achieved, as assumed throughout this thesis.

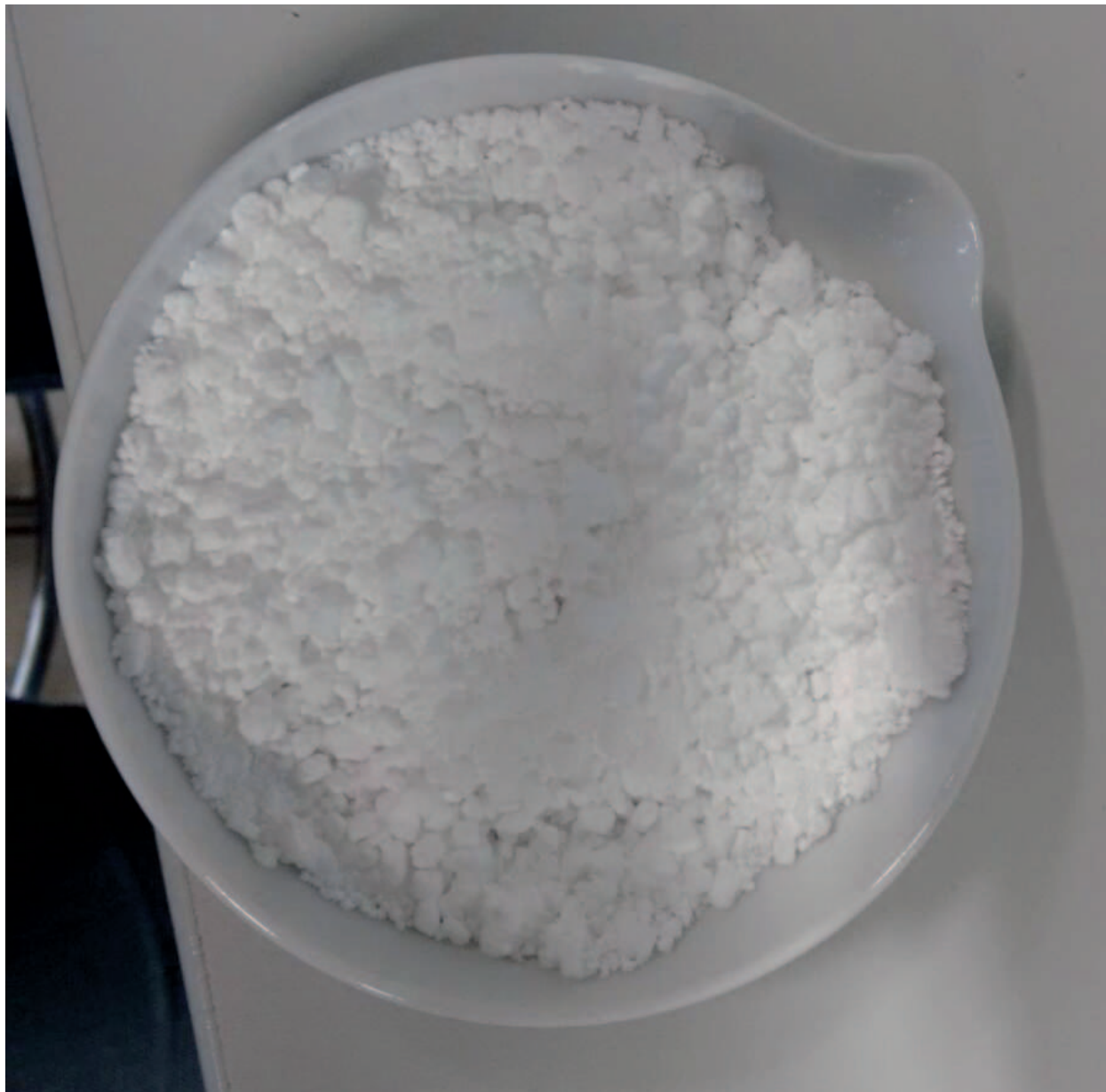


Figure 6.1: Dried boric acid. This product was produced in MIBK, filtered and then dried in a vacuum oven until weight constant.

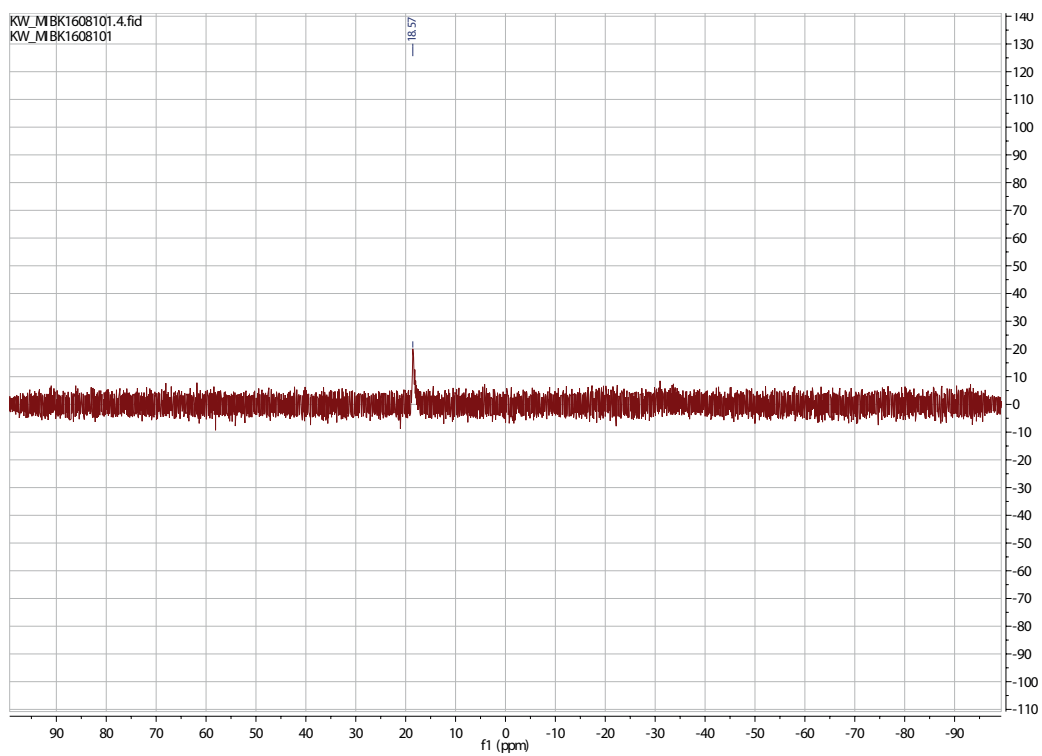


Figure 6.2: NMR of boric acid solvated in MIBK.

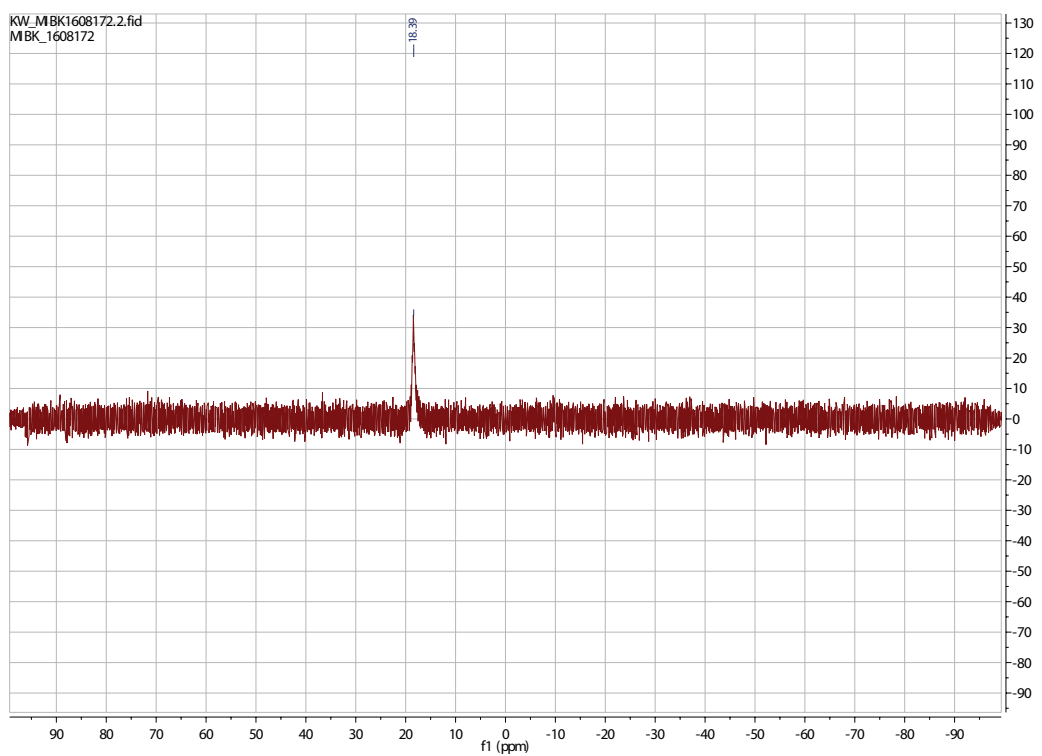


Figure 6.3: NMR of the reaction product in MIBK.

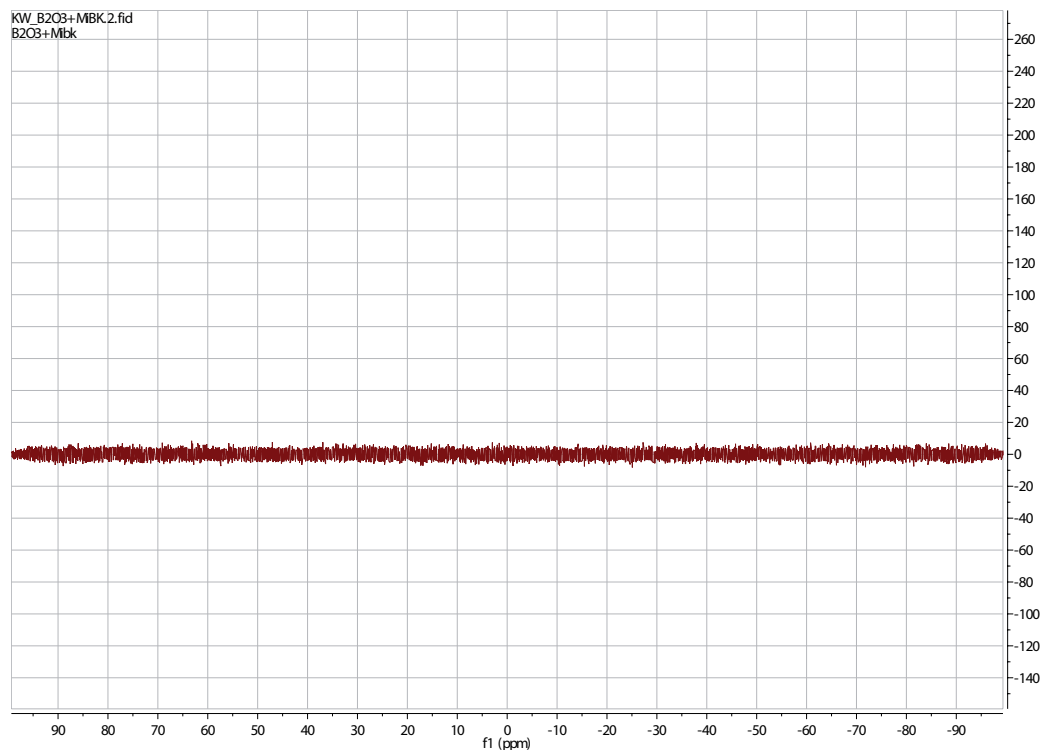


Figure 6.4: NMR of the reaction product in MIBK.

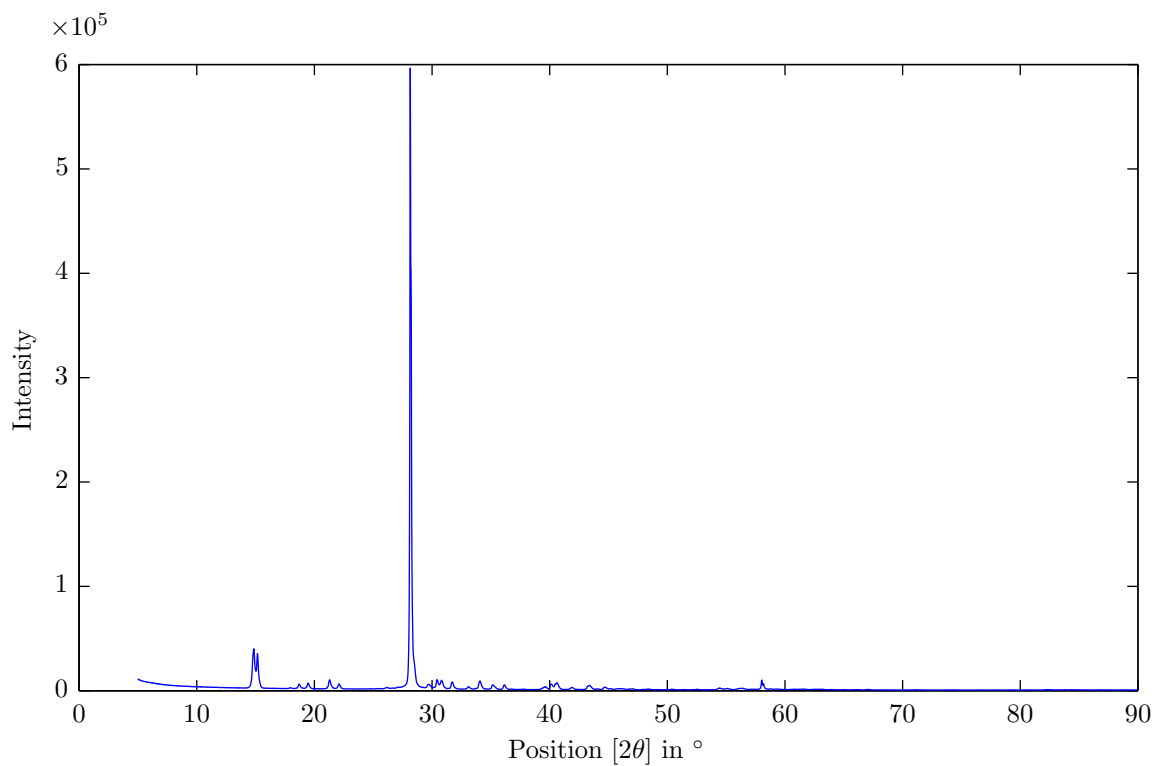


Figure 6.5: XRD of reaction product.



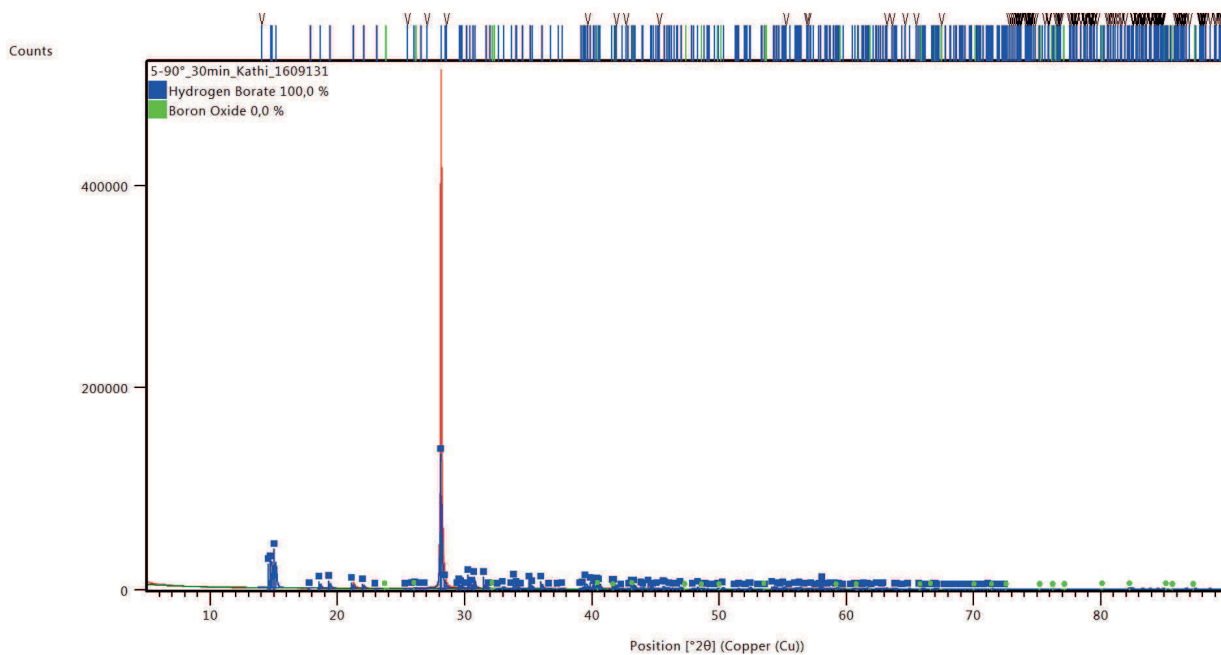


Figure 6.6: XRD of reaction product. Hydrogen borate describes boric acid in the legends used in this figure. This XRD shows that only boric acid remains after the reaction.

### 6.3 Temperature dependency

The experiments done according to 4.6.2 lead to figure 6.7. This figure shows that the reaction goes faster, the higher the starting temperature. The only exception are the curves for 2 °C and 10 °C. For 10 °C the initial reaction rate is faster to 2 °C but a total conversion is reached earlier if a starting temperature of 2 °C was applied.

The trend of a faster reaction can also be seen if  $t_{50}$  is compared. Only the measurements at 25 °C do not follow this trend. This might be due to the slightly different experimental setup. Since the experiments at 25 °C were performed at room temperature, the water was not checked for its starting temperature. The water was stored outside the fume hood so it might be possible, that the water has a different temperature, influencing the reaction. The trend seen in figure 6.8a also shows that there is a statistically relevant difference for the reactions at 10 and 60 °C. The measurements at 2 °C did not give a statistically relevant difference, since the standard deviation is too big for this experiment.

The efficiency, seen in figure 6.8b shows a similar trend. The higher the starting temperature, the lower the efficiency. This might be because the heat loss is bigger at higher temperatures and since higher maximal temperatures were reached for higher starting temperatures, this correlates to the findings. But it can also be seen again, that the measurements at 25 °C are not corresponding with the other measurements.

### 6.4 Mass dependency

Changing the ratio between  $B_2O_3$  and MIBK while keeping  $\lambda$  constant lead to the revelation that the beforehand used concentration is already close to the maximal usable solid content. Therefore the experiments listed in table 4.7 could only partially lead to satisfying results. If

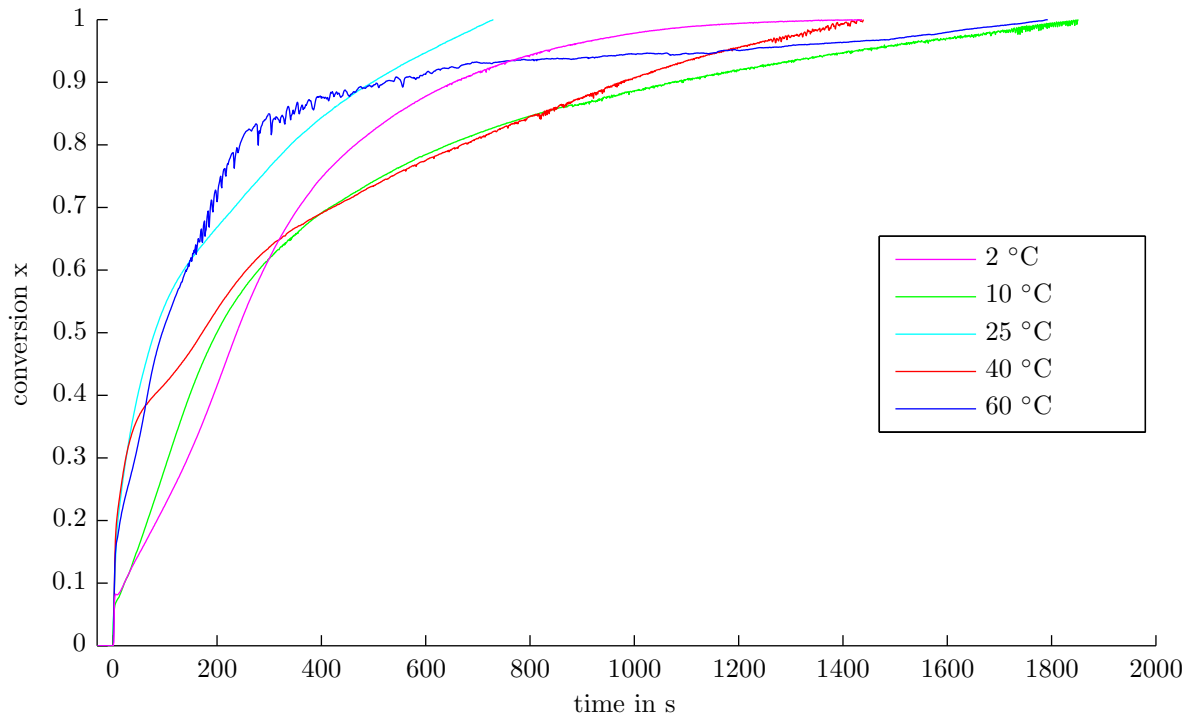


Figure 6.7: Dependency of the conversion for various starting temperatures

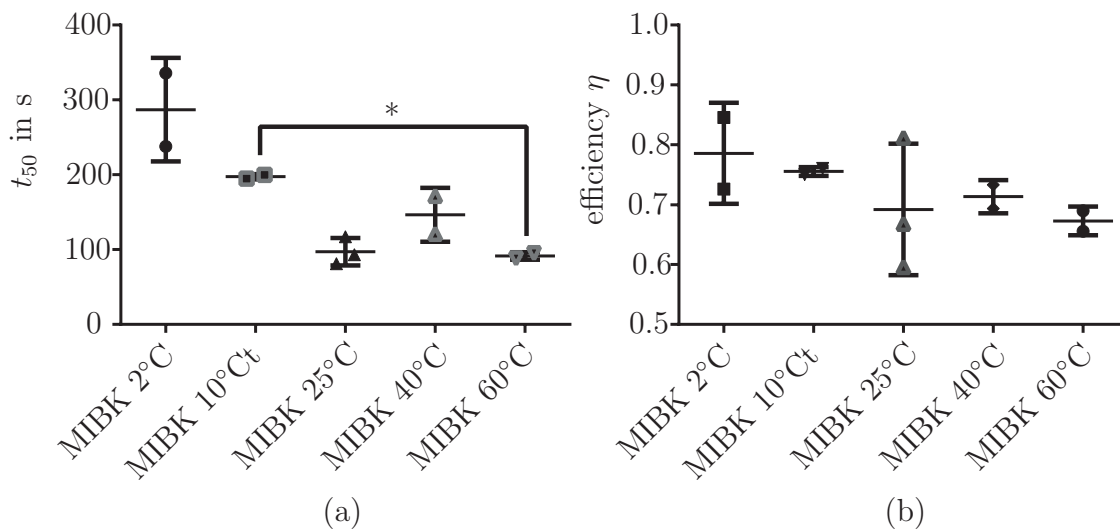


Figure 6.8: The graphs show the experiments in MIBK for different starting temperatures. It depicts the average value and the standard deviation. (a) shows  $t_{50}$  and (b) the efficiency of the system.

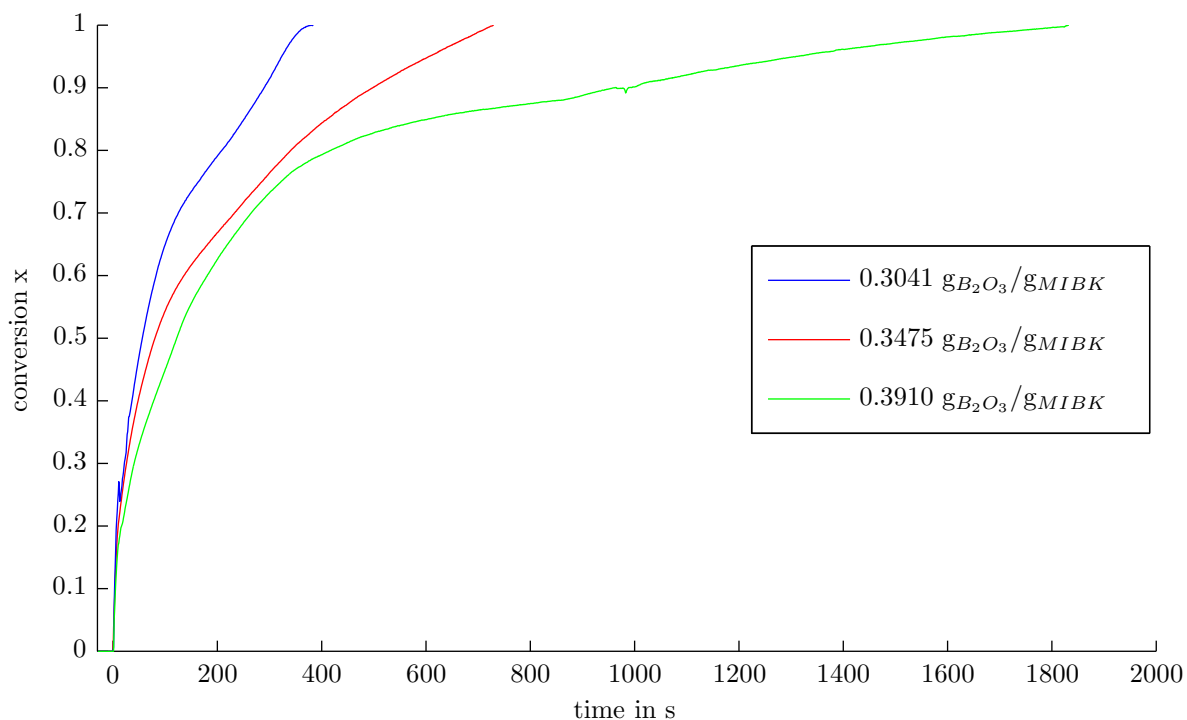


Figure 6.9: Dependency of the conversion for various mass relationships

too much solid was used, the stirrability decreased and a homogeneous mixture could not be guaranteed any more. Therefore only the values for a ratio of 0.875, 1 and 1.125 are shown in figure 6.9.

Studying  $t_{50}$  and the efficiency, figure 6.10, shows again that the reference measurement does not fit into the trend. The reaction time increases for more solids; this might be due to an increased viscosity making it harder to obtain a homogeneously mixed reaction. Also the efficiency increases for higher solid amounts since the losses are a constant value independent of the amount inside the reactor. Therefore the relative losses are less if more boron trioxide can react to boric acid.

## 6.5 Reaction with and without solvent

Figure 6.11 compares the conversion for several reactions with the same liquid:solid ratio. The experiments in solvent are conducted with  $\lambda=1.5$  and  $B_2O_3$  first in this works reactor and in Hashemi's reactor. Another experiment was conducted, where MIBK was substituted by the same mass of water, leading to  $\lambda = 5$  for this reaction. The reaction in water has the a similar reaction time as the reaction in MIBK in this works reactor. If Hashemi's reactor is used for reactions with a solvent, the reaction is even faster, compared with the other two cases.

The temperature increase during the reaction is depicted in figure 6.12. If water is used as a solvent, the temperature increases faster, but the reached end temperature is higher if a solvent is used, especially if the experiment is performed in Hashemi's reactor.

However, the experiments in Hashemi's reactor are not as reproducible as in the reactor used in this study. This might be due to a worse mixing inside the reactor which leads

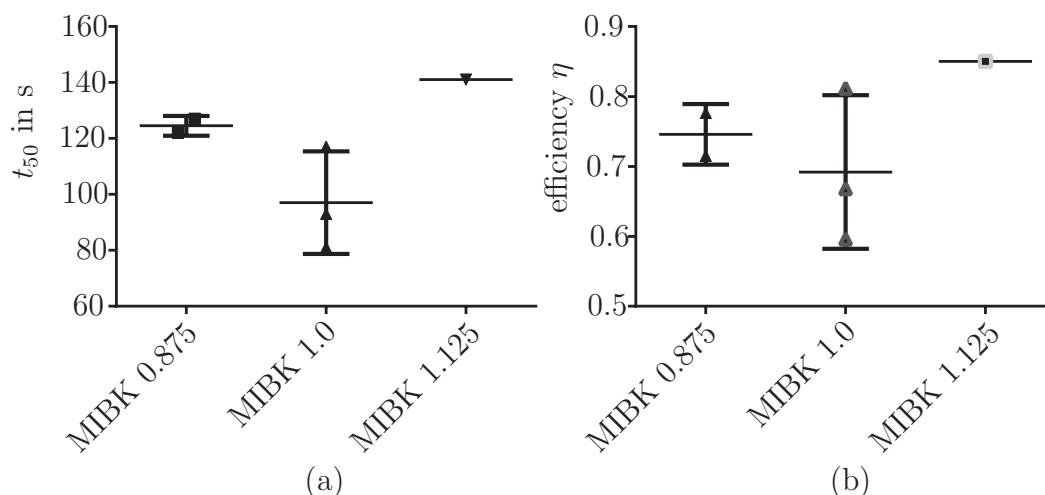


Figure 6.10: The graphs show the experiments in MIBK for different solid masses. It depicts the average value and the standard deviation. (a) shows  $t_{50}$  and (b) the efficiency of the system.

to inhomogeneity and heat spots. Also it was necessary to perform the experiments in the standard reactor to be able to compare them with solvents that evaporated during the reaction.

In figure 6.13 the reaction start is enlarged. It shows that in the first seconds of the reaction the conversion behaves the same way in both reactors. Only later on the reaction progresses faster inside Hashemi's reactor.

Furthermore, in figure 6.13 it is visible that the equipment used to measure the temperature in Hashemi's reactor is not as exact as the measurement method for the normal reactor. This discrepancy can be seen in the steps that are visible in the conversion curves. Since the time resolution of one second is the same for both measurement methods, the reason for the worse smoothness is the resolution in temperature. The thermocouple temperature logger used in Hashemi's reactor has a resolution of  $0.1 \text{ }^\circ\text{C}$ . On the other hand, the measuring board used in the normal reactor has a resolution of  $1 \cdot 10^{-4} \text{ }^\circ\text{C}$ .

A further comparison is possible if  $t_{50}$  and  $\eta$  are compared. This is done in figure 6.14. It is visible that the reactor does not have a relevant influence on  $t_{50}$  and  $\eta$  if a solvent is used in both cases. But as already mentioned before the reaction occurs faster than without a solvent. The efficiency with water as the solvent is higher.

This is further summarized in table 6.1, where it is visible, that the energy produced is higher in water, with a decrease in the maximal temperature. Therefore, it is necessary to decide, whether the temperature or the energy output is the more important criterion.

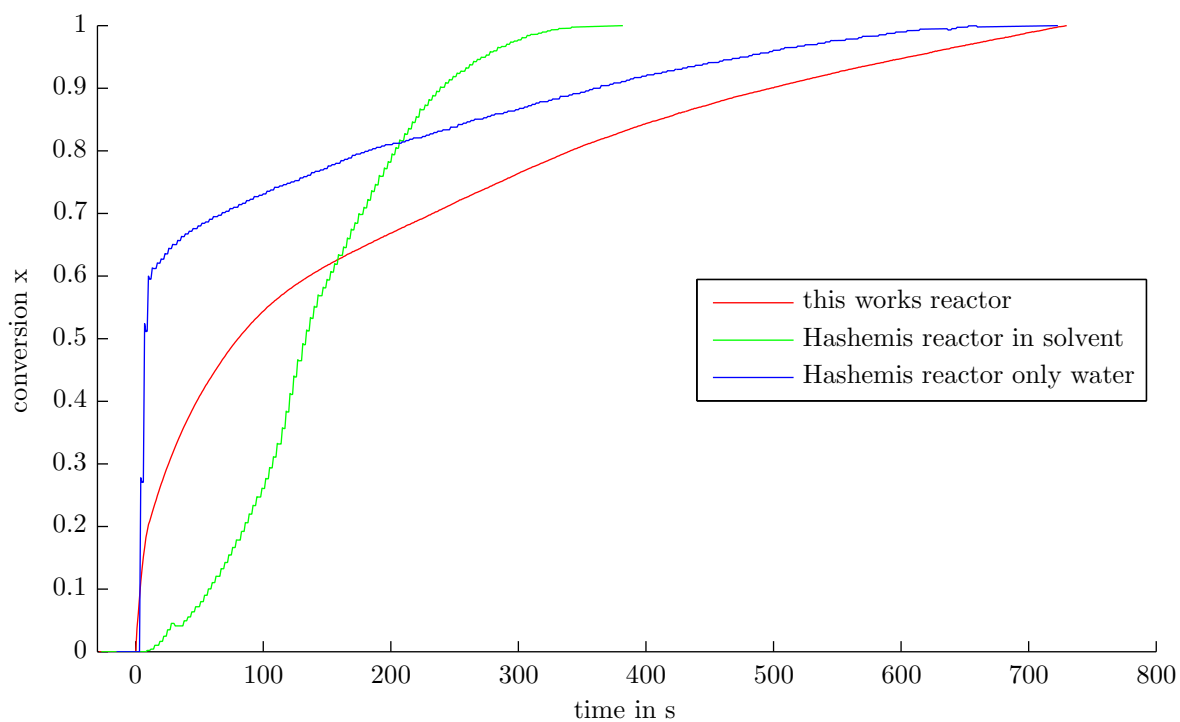


Figure 6.11: Compares the conversion in water with reactions, where some of the water is substituted with solvent. The mass of liquid is kept constant.

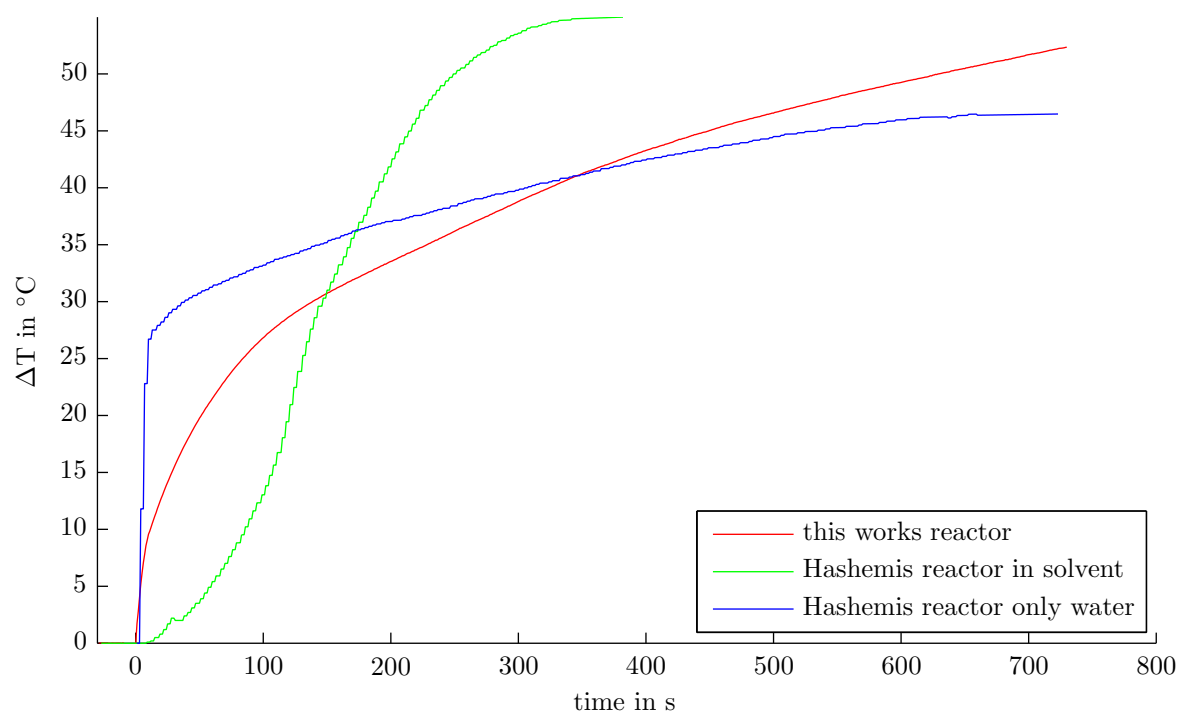


Figure 6.12: Compares the temperature increase in water with reactions, where some of the water is substituted with solvent. The mass of liquid is kept constant.

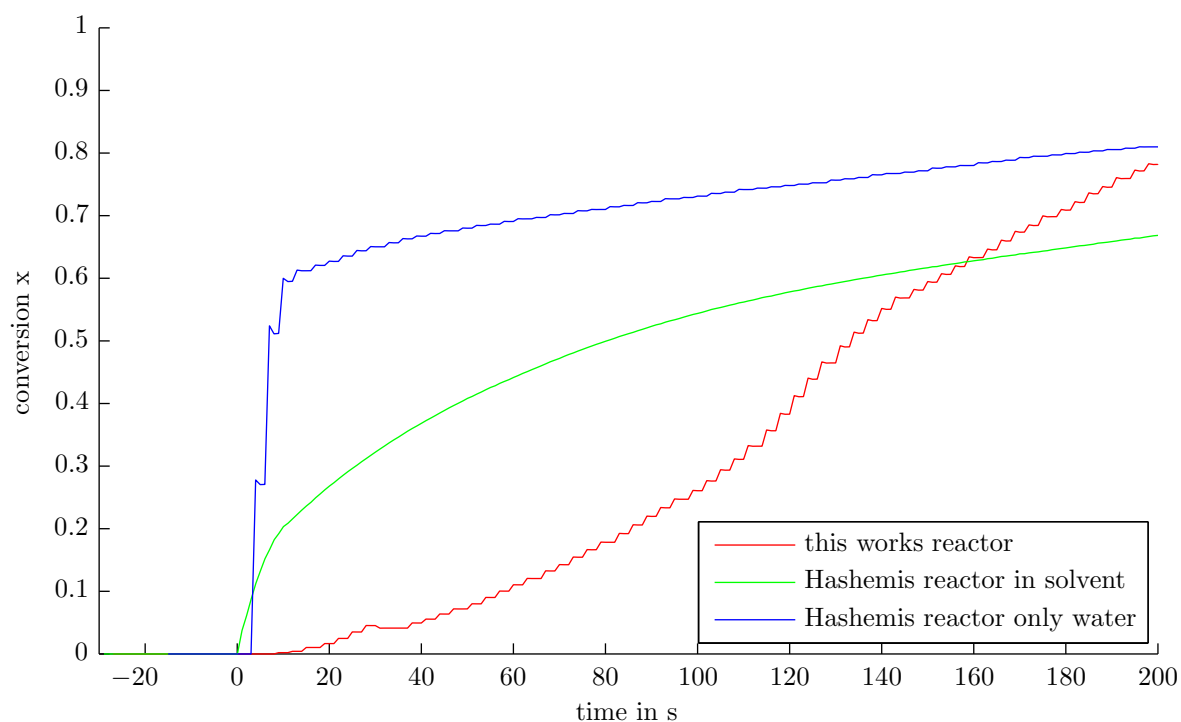


Figure 6.13: Compares the conversion in water with reactions, where some of the water is substituted with solvent, zoomed in on the reaction start. The mass of liquid is kept constant.

Table 6.1: Maximal reached temperature and energy produced in MIBK and water

	reaction in this works reactor with solvent	reaction with solvent in Hashemi's reactor	reaction with water in Hashemi's reactor
maximal reached temperature in K	351.99	356.04	346.53
produced heat in $\frac{kJ}{kgB_2O_3}$	539.12	570.40	727.66

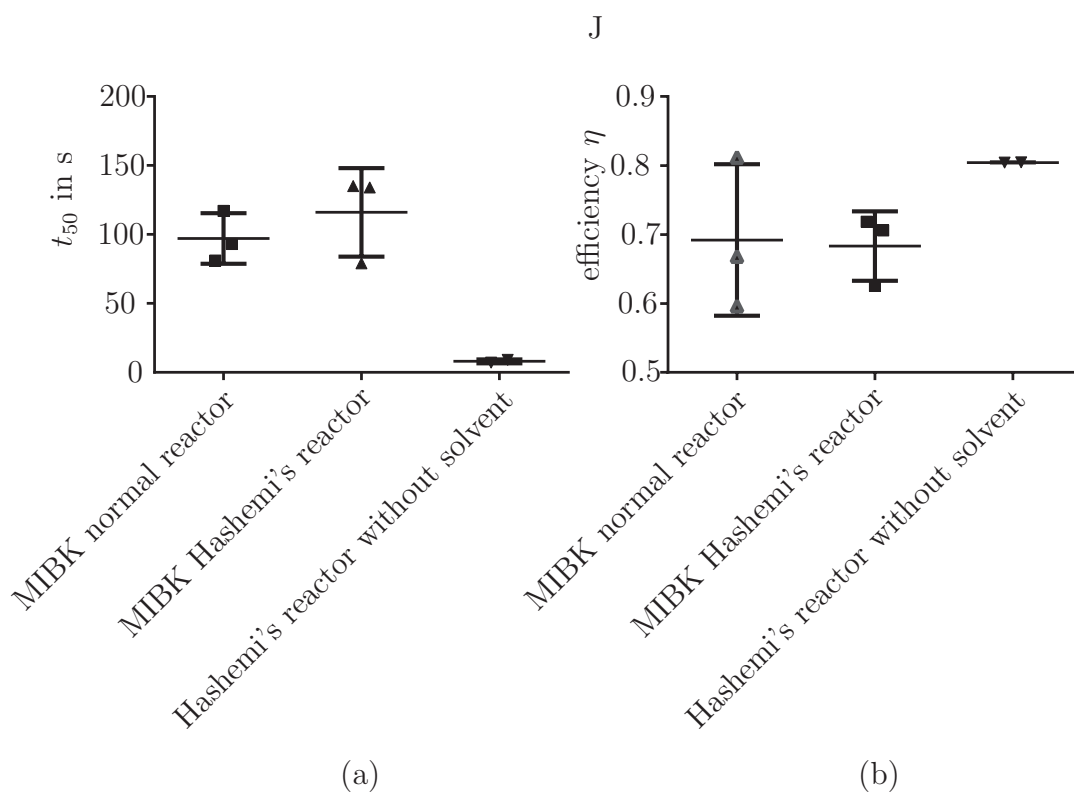


Figure 6.14: The graphs show the experiments in MIBK in both used reactors and the reaction without solvent in Hashemi's reactor. It depicts the average value and the standard deviation. (a) shows  $t_{50}$  and (b) the efficiency of the system.





# Chapter 7

## Conclusion and outlook

### 7.1 Using different solvents for the reaction from $B_2O_3$ to $H_3BO_3$

In this work several solvents were tested for their possibility as a suspension medium for the reaction of boron oxide to boric acid. Several tests showed that alcohols are not suitable solvents since they react with boron oxide, and also boric acid, to form boron esters. These esters were checked for their suitability as a new TCES. The storable heat per kg boron oxide was lower than the storable heat in the system  $B_2O_3/H_3BO_3$ . Another disadvantage is their instability even if they are just exposed to air humidity. Additionally, they are hard to purify. All these criteria lead to the decision that boron esters were not added as new candidates as a TCES system.

Using low boiling solvents also did not give the wanted outcome. At least in the setup tested throughout this thesis the evaporation of part of the solvent was not wanted. Otherwise, these solvents could still be used in the end to set a certain working temperature. Therefore, low boiling solvents might be tested again in the future.

The last two solvents studied were heptane and MIBK. Both of them exhibited some problems, since the miscibility of water and the solvents was low. That is the reason why the liquid and the solid separated during the start of the reaction and only combined again after some time. But in the end MIBK was chosen for a more detailed analysis since this separation was more prevalent in heptane than in MIBK.

### 7.2 MIBK as a solvent for the reaction of water and boron oxide

A further analysis studied the reaction in MIBK in more detail. The experiments showed that the reaction is faster, if the starting temperature is increased, but with a slightly reduced efficiency. An increase of reacting mass, on the other hand, lead to a slower reaction with a higher efficiency.

Comparing the experiments to an experiment, where the solvent is substituted back with water, the wanted goal can be achieved. The observed temperature increase is higher in MIBK and therefore justified this work.

Regarding the purification it was possible to dry the produced boric acid sufficiently to use

it for the energy storage step already optimized by Karel [21].

## 7.3 Outlook

This work shows that it is possible to increase the maximal temperature of the reaction of boron oxide to boric acid. This can be explained by the lower heat capacity of MIBK, compared to the heat capacity of water.

To be able to further study this kind of reactions it would be advisable to develop a process, which can be compared to a process, where only water is used. As soon as a running process is established, further studies with more solvents are possible, that can be immediately compared to a process in water. Especially polar higher boiling solvents should be one of the solvents tested to better cover all types of solvents.

If only the hydration is done in suspension, then it is necessary to evaluate the energy demand to separate the product boric acid from the solvent. In this approach the dehydration would be done in the setup established by Karel [21].

Summing up, this work gives a first overview of the challenges regarding the reaction of boron oxide to boric acid in different solvents.

# Chapter 8

## Abbreviations

Abbreviation	meaning
AA-CAES	advance adiabatic compressed air energy storage
CAES	compressed air energy storage
ES	energy storage
FES	flywheel energy storage
LHS	latent heat storage
MIBK	methyl isobutyl ketone
PHES	pumped hydro energy storage
SHS	sensible heat storage
TEG	triethylene glycole
TES	thermal energy storage



# Chapter 9

## Nomenclature

Table 9.1: Nomenclature

variable	Unit	Description
$\alpha$	$\frac{C \cdot m^2}{V}$	polarizability
$c_p$	$\frac{J}{mol \cdot K}$	heat capacity
$c_{p,total}$	$\frac{J}{mol \cdot K}$	total heat capacity
$\Delta H$	$\frac{J}{mol}$	enthalpy of formation
$\Delta H^P$	$\frac{J}{mol}$	heat of phase change
$\Delta H_R$	$\frac{J}{mol}$	reaction enthalpy
$\epsilon_r$	1	relative permittivity
$H^0$	$\frac{J}{mol}$	standard enthalpy of formation
$H$	$\frac{J}{mol}$	produced enthalpy
$\eta$	1	efficiency
$m_{B_2O_3}$	g	boron oxide mass
$m_{Ester}$	g	ester mass
$m_{H_2O}$	g	water mass
$m_{H_2O,added}$	g	water added to the mixture
$m_{H_2O,used}$	g	water used up during reaction
$m_{H_2O,solvent}$	g	water in solvent
$m_{H_2O,stoichiometric}$	g	water necessary for reaction
$m_{H_2O,ROH}$	g	water in the alcohol
$m_{ROH}$	g	mass of alcohol
$m_{solvent}$	g	solvent mass
$m_{total}$	g	total liquid mass
$M_{B_2O_3}$	g/mol	molar mass of boron oxide
$M_{H_2O}$	g/mol	molar mass of water
$M_{ROH}$	g/mol	molar mass of alcohol
$n_{B_2O_3}$	mol	moles of boron oxide
$n_{Ester}$	mol	moles of produced ester
$n_{H_2O}$	mol	moles of water
$n_{H_2O,ROH}$	mol	moles of water in the alcohol
$n_{H_3BO_3}$	mol	moles of boric acid
$n_{MIBK}$	mol	moles of MIBK
$n_r$	mol	reacted moles

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$n_{ROH}$	mol	moles of alcohol
$\nu$	$m^2/s$	viscosity
$\nu_i$	-	stoichiometric factor of species i
$\dot{q}_{loss}$	J/s	heat loss rate
$Q_{loss}(t)$	J	heat lost until time t
$Q_R$	J	maximal produced heat
$t$	s	time
$t_{end}$	s	end time of reaction
$t_0$	s	start of reaction
$t_{50}$	s	time when x=0.5 is reached
$T$	K	temperature
$T_0$	K	25 °C
$T_{ad}$	K	adiabatic temperature
$T_p$	K	phase change temperature
$T_{start}$	K	temperature at $t_{start}$
$w$	1	water content
$x$	1	conversion

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# Appendix

## A.1 tables

Table 1: titration results for methanol and ethanol experiments. Furthermore, conversion calculations for the esterification of ethanol and boric acid are included.

experiment	Methanol2	EthanolB
titration before in weight/%	0	5.802
weighted alcohol in g	23.0702	46.770
water content before in g	0.000	2.714
$n_{H_2O,1}$	0.000	0.151
amount of alcohol	23.070	44.057
$n_{ROH,1}$	0.501	0.956
added $B_2O_3$ ,	9.694	
$n_{B_2O_3}$	0.139	
added $H_3BO_3$		31.663
$n_{H_3BO_3}$		0.512
titration after reaction in weight/%	16.083	12.263
n_reacted		0.160
water content after reaction		5.590
consumed water in g		2.876
stoichiometric water usage		17.228
conversion x		0.16

Table 2: Conversion calculations when assuming that the hydrolysed product is boric acid. The experiment parameters are taken from table 4.2. The values were calculated according to equations 3.3-3.14

experiment	TEG1	TEG2	TEG3	TEG4	TEG5	TEG6	TEG7	TEG8	TEG9	TEG10	TEG11	TEG12
titration before in weight/%	0.388	0.363	0.342	0.335	0.387	0.322	0.350	0.317	0.377	0.315	0.342	0.313
weighted TEG in g	29.694	30.280	29.807	31.539	31.452	30.820	29.426	23.573	29.787	31.488	19.678	18.900
water content before in g	0.115	0.110	0.102	0.106	0.122	0.099	0.103	0.075	0.112	0.099	0.067	0.059
amount of TEG in g	29.578	30.170	29.705	31.433	31.331	30.721	29.323	23.498	29.675	31.388	19.610	18.841
added water	19.198	20.107	18.631	31.632	31.259	30.045	57.878	60.363	58.529	61.798	66.897	61.617
total water be- fore reaction	19.313	20.217	18.733	31.738	31.381	30.144	57.981	60.437	58.641	61.898	66.964	61.676
titration af- ter reaction in weight/%	12.197	12.420	12.060	27.683	23.457	21.680	59.605	62.857	54.673	56.730	73.227	71.803
water content af- ter reaction	3.622	3.761	3.595	8.731	7.378	6.682	17.540	14.817	16.285	17.863	14.409	13.571
consumed water	15.576	16.346	15.036	22.901	23.881	23.363	40.338	45.545	42.243	43.935	52.488	48.047
added $B_2O_3$	25.089	25.940	25.430	26.686	26.443	25.883	24.720	20.393	25.202	26.661	17.151	16.102
stoichiometric water usage	19.476	20.137	19.742	20.716	20.528	20.093	19.190	15.831	19.564	20.697	13.315	12.500
conversion x	0.79	0.81	0.76	1.10	1.16	1.16	2.10	2.87	2.15	2.12	3.94	3.84

Table 3: Conversion calculations for ethyl acetate

experiment	Ethyl acetate 1	Ethyl acetate 2
titration before reaction in ppm	730.500	736.767
water content before reaction in g	0.039	0.039
amount of ethyl acetate	52.885	52.598
added water	16.063	16.120
total water before reaction	16.101	16.159
titration after reaction in weight%	2.213	2.088
water content after reaction	1.171	1.099
consumed water	14.891	15.021
stoichiometric water usage	16.433	16.171
conversion x	0.90	0.92

Table 4: Conversion calculations in heptane with the results of Karl-Fischer titration.

experiment	Heptan2	Heptan3	Heptan4	Heptan5
titration before in ppm	25.663	27.885	40.135	39.780
weighted heptane in g	39.825	40.061	40.040	39.586
water content heptane in g	0.001	0.001	0.002	0.002
amount of heptane	39.823	40.060	40.039	39.584
added water	10.671	10.799	10.687	15.861
total water before reaction	10.672	10.800	10.688	15.862
titration after reaction in ppm	38.970	40.133	39.593	108.223
water content after reaction	0.002	0.002	0.002	0.004
consumed water	10.669	10.797	10.685	15.856
added $B_2O_3$	14.142	14.089	14.034	13.782
stoichiometric water usage	10.978	10.937	10.895	10.699
conversion x	0.97	0.98	0.98	1.48

Table 5: Results for the drying experiments.

Experiment	1608172	1608181	1609131
MIBK	31.7871	31.9708	32.0199
$B_2O_3$	11.0708	11.1851	11.0943
$H_2O$	12.8016	12.9215	12.8570
$H_3BO_3$	19.6641	19.8671	19.7058
Liquid in g	35.9954	36.2103	36.2654
Total mass in g	55.6595	56.0774	55.9712
Mass added to filtration	50.8370	54.9600	54.9230
Corrected expected solid mass	17.9604	19.4713	19.3368
Liquid in Büchner flask in g	9.08	9.92	10.97
filtered wet solid	24.3168	23.0522	26.5910
Vacuum drying oven	17.3615	19.5338	18.5459
fluid part in weight%	28.60	15.26	30.25