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Dissertation

Thermochemical energy storage on the basis of boric acid and copper oxide- towards a sustainable energy provision

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I acknowledge that publication of this thesis requires the approval of the examination committee.

Affidavit

I declare in lieu of oath, that this thesis and the work presented in it are my own and have been generated by me as the result of my own research, using only literature cited in this volume. Where I have quoted text passages from the work of others, the source is always given and clearly attributed.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna, February 2020

Clemens Huber

Abstract

Energy and life are inevitably interlinked with each other. While life without energy is impossible, an excess of energy is equally dangerous and harmful. Paracelsus already recognised, that it is the dose that makes the poison, and it appears as if mankind is still struggling to find the appropriate and healthy dose of energy for itself and the environment. The consequence of humanity's excessive energy hunger, the greenhouse effect, has become a global threat and can only be confronted by a reasonable, sustainable and efficient use of energy. Harnessing renewable energy sources is one promising way of providing energy without harmful emissions or further adverse impacts on the environment. However, the energy provision of such energy sources is inconsistent, depending on various influencing factors (time, location, weather...), and is mostly incapable of matching the actual energy demand. As a result, global energy only consists of a small share of renewable energy sources and a big share of fossil fuels. Thermochemical energy storage (TCES) can offer a solution to the current problem, by bridging the gap between sustainable energy provision and energy demand, thereby supporting the usage of renewable energy sources. Two promising reaction systems were analysed regarding their suitability as thermochemical energy storage. The findings revealed the reaction systems' respective characteristics, kinetics and influencing factors on the reaction, as well as their existing challenging properties, calling for further research and improvement. This work therefore, meaningfully contributes to further research in the field of thermochemical energy storage and a sustainable energy provision based on renewable energy sources.

Kurzfassung

Leben und Energie sind zweifellos miteinander verbunden. Während ohne Energie kein Leben möglich ist, ist auch ein Überschuss davon schädlich. Paracelsus erkannte bereits, dass es die Dosis sei, die das Gift ausmache. Dieser Schluss trifft auch auf den Umgang mit Energie zu und hier scheint der Mensch hinsichtlich der richtigen Dosis, sowohl für sich selbst, als auch die Umwelt noch keine entsprechende Balance gefunden zu haben. Als Konsequenz des stetig ansteigenden Energiehungers der Menschheit hat sich der Treibhausgaseffekt zu einer globalen Gefahr entwickelt. Nur mehr ein angemessener, nachhaltiger und effizienter Umgang der Menschen mit Energie kann hierbei mittlerweile Abhilfe schaffen. Diesbezüglich ist eine Energieversorgung basierend auf erneuerbare Energiequellen ohne schädliche Emissionen und ökologischen Fußabdruck das mittel erste Wahl. Leider sind diese Energiequellen derzeit aufgrund von verschiedenen Einflussfaktoren (Wetter, Zeit, Ort...) auf die Energiebereitstellung nur sehr eingeschränkt nutzbar. Die unstete Bereitstellung von Energie passt zudem meist nicht zum tatsächlichen Verbrauch, weshalb viel dieser Energie ungenutzt bleibt. Dementsprechend, nehmen erneuerbare Energiequellen nur einen minimalen Teil am Gesamtenergiemix ein, der Großteil wird immer noch durch fossile Energiequellen bereitgestellt. Thermochemische Energiespeicher (TCES) können hierbei Abhilfe schaffen und die Nutzung nachhaltiger Energie unterstützen. TCES können als Speichertechnologie nachhaltige Energie mit dem Verbrauch koppeln und so verhindern, dass auf andere nicht nachhaltige Energiequellen zurückgegriffen werden muss. Im Rahmen dieser Arbeit wurden zwei vielversprechende Reaktionssysteme, hinsichtlich ihrer Eignung zur Speicherung von thermischer Energie, näher untersucht. Dabei konnten Reaktionseigenschaften, die Kinetik der Reaktion und Einflussfaktoren auf die Reaktion sowie stoffspezifische Herausforderungen, welche noch weiter erforscht werden müssen, festgestellt werden. Diese Arbeit trägt durch die Ergebnisse somit substantiell zur weiteren Forschung auf dem Gebiet der thermochemischen Energiespeicherung und einer hoffentlich nachhaltigen zukünftigen Energieversorgung bei.

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Diese Arbeit widmet sich dem Thema Energie und dem nachhaltigen Umgang damit. Aus diesem Grund finde ich es passend, für die Worte an dieser Stelle, gleich dabei zu bleiben. Energie bedeutet Leben und ist damit ein essentieller Bestandteil der Menschheit. Energie, ist Arbeit und Arbeit über Zeit ist Leistung. Leistung ist es, die mich in meinem Leben an diesen Punkt, hier zum Abschluss meiner Dissertation, gebracht hat. Ebenso war es die Leistung vieler wunderbarer Menschen, die mich im Laufe meines Lebens durch ihren Einsatz nachhaltig unterstützt haben und so dazu beigetragen haben, dass ich heute an der Schwelle zu einem neuen Lebensabschnitt stehe. Theodor Heuss hat einmal gesagt „Nur wer weiß, woher er kommt, weiß, wohin er geht“. Ich finde das sehr passend, denn das Leben ist viel zu fragil um es nur fokussiert auf das Hier und Jetzt zu genießen, zu beachten und zu schätzen. Aus diesem Grund möchte ich die Möglichkeit nutzen um zurückzublicken und für all die Unterstützung, die mir bisher im Laufe meines Lebens wiederfahren ist, danke zu sage.

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List of papers included in this thesis

- I. Huber, C., Jahromy, S. S., Birkelbach, F., Weber, J., Jordan, C., Schreiner, M., . . . Winter, F. (2020). The multistep decomposition of boric acid. Energy Science & Engineering, n/a(n/a). doi:10.1002/ese3.622
- II. Huber, C.; Setoodeh Jahromy, S.; Jordan, C.; Schreiner, M.; Harasek, M.; Werner, A.; Winter, F. Boric Acid: A High Potential Candidate for Thermochemical Energy Storage. Energies 2019, 12, 1086.
- III. Setoodeh Jahromy, S.; Birkelbach, F.; Jordan, C.; Huber, C.; Harasek, M.; Werner, A.; Winter, F. Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu₂O to CuO in Thermochemical Energy Storage. Energies 2019, 12, 508.

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- I. **Author Contributions:** Conceptualisation, C.H.; Data curation, C.H.; Formal analysis, C.H., and S.S.J.; Investigation, C.H., S.S.J. and C.J.; Methodology, C.H., F.B. and S.S.J.; Project administration, M.H., M.S. and F.W.; Resources, S.S.J., M.H., M.S. and F.W.; Software, C.H., F.B., J.W. and S.S.J.; Supervision, M.H., M.S. and F.W.; Validation, S.S.J. and C.J.; Visualisation, C.H.; Writing-original draft, C.H.; Writing-review & editing, C.H., S.S.J., C.J., M.S. and F.W.

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1. Introduction

1.1. The current problem

Energy is powering our world, it can be universally found at any point in time and, because of the basic law of conservation energy, can neither be created nor can be destroyed. Humanity is in constant daily contact with different co-existing forms of energy, such as: thermal, electrical, chemical and nuclear, as well as potential or kinetic energy. The countless number of electronic devices or products used by humans every single day, demonstrates that energy has become an indispensable need in everyday life. The main problem is that the current predominant energy sources are fossil based and are causing manifold harmful emissions with serious consequences for the environment. The future energy supply should therefore be based on renewable sources, to enable a considerable cut of emissions. However, due to their intrinsic properties, these sources are still not capable of fulfilling the expectations. Thermochemical energy storages are considered a new approach to promote the thermal energy provision through renewable energy sources by reducing the consequences of the greenhouse effect.

In 2016, 80% of the consumed primary energy (160 PWh) was covered by fossil fuels (Figure 1), leading to CO₂ emissions of 32.1 Gt. With a share of only 16% of the global energy mix, renewable energy sources only played a minor role in 2016.

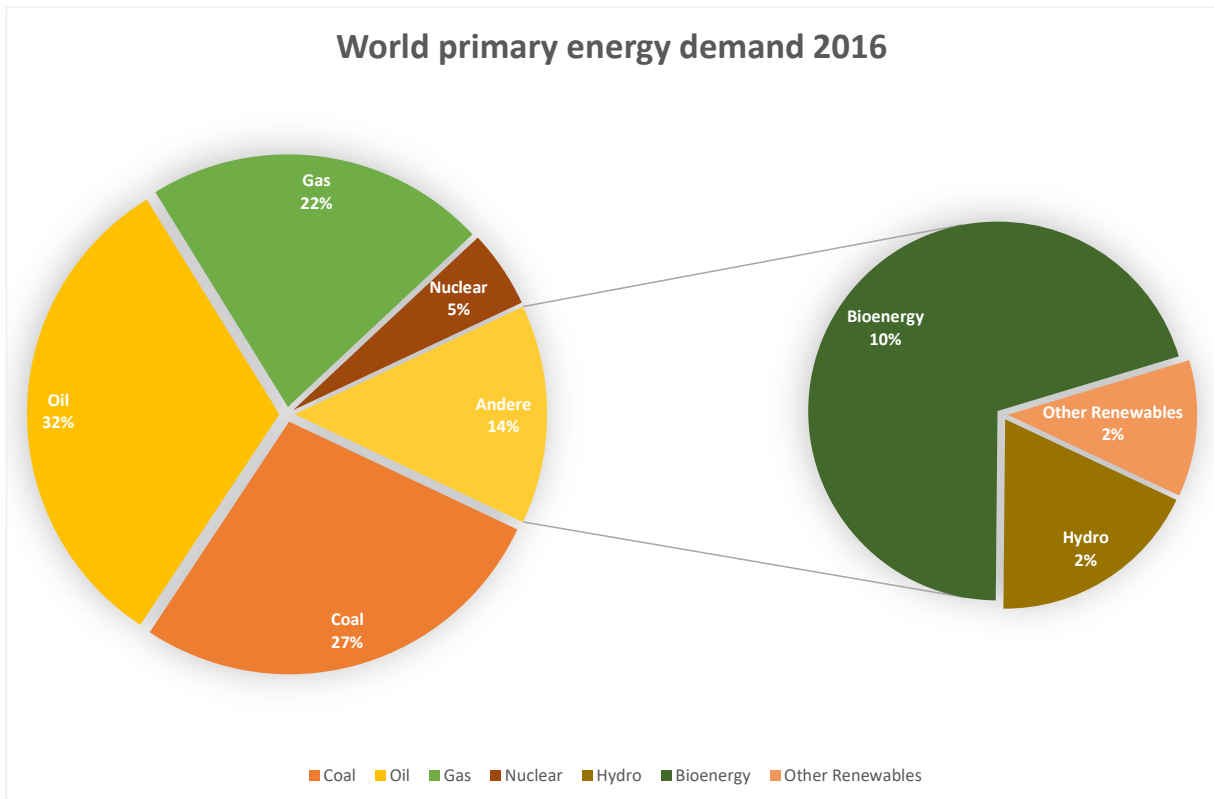


Figure 1 Sources of primary energy in 2016 (International Energy Agency, 2017)

Initiated by the industrial revolution, the steadily increasing need for energy was predominantly covered through fossil fuels, with severe consequences, such as increasing air pollution via greenhouse gas emissions (CO₂, CH₄, NO_x, H-CFCs and Vapour) (Figure 2). While western industrial cities continuously drowned in clouds of smog, air pollution remained an underestimated and hardly considered issue until the end of the last millennium. Nevertheless, its negative impact on the world's climate can no longer be ignored. Nowadays, the far-reaching consequences, like the global temperature rise of 1.6 degrees since the 19th century, ocean warming, shrinking ice sheets, glacial retreat, sea level rising or extreme weather events, are omnipresent and the question of how to tackle the problems related to air pollution has turned into a global topic.

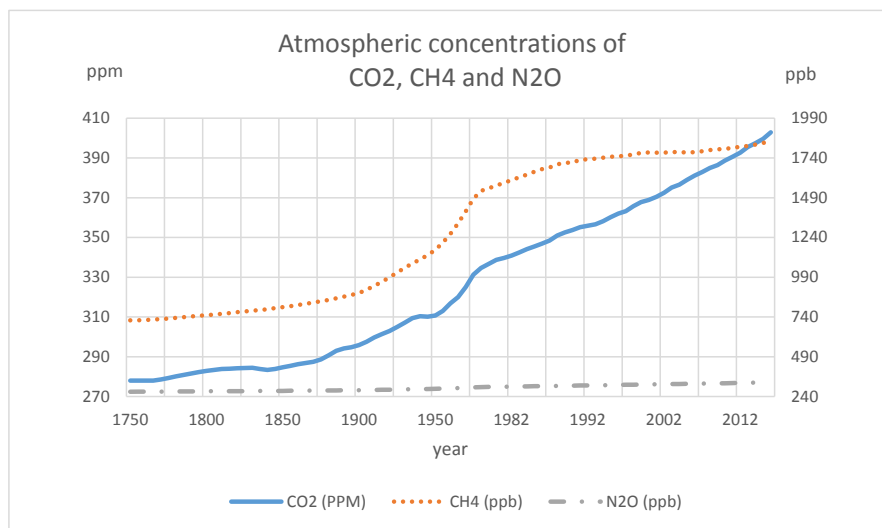


Figure 2 Atmospheric concentrations of CO₂, CH₄ and N₂O from 1800 to 2015 (European Environment Agency, 2019)

The ecological footprint is a good way to visualise the overexploitation of natural resources by mankind. Although the concept is often criticised for some indistinctness and for being oversimplified, it is still suitable to illustrate the vital importance of global sustainability. A value bigger than one, refers to a human way of life that exceeds the amount of natural resources available.

For carbon dioxide emissions, the ecological footprint analyses the ratio between existing natural resources and actual needed resources, regarding the ability to fully degrade the amount of globally produced CO₂. Currently, humanity would therefore need the resources of 1.7 earths. By looking at statistics concerning the expected future energy demand, the need for a global energy revolution can no longer be denied (Global Footprint Network, 2019).

The impact of greenhouse gas (GHG) emissions on the atmosphere was already discovered in the 19th century. Researchers like Jean Baptiste Joseph Fourier, John Tyndall or Svante Arrhenius become aware of the greenhouse effect and its consequences by predicting a rise of the earth's surface temperature due to increasing carbon dioxide levels (Weart, 2019, Ramanathan and Andrew, 1997, Archer and Pierrehumbert, 2013). However, it took politics until the 20th century, to become fully

conscious of the threat of global warming and its harmful impact on the world. The Kyoto Protocol, subsequently became the first international agreement with the aim to protect the environment. Nowadays there are several international attempts to cut down GHG emissions, in order to reduce the further global warming progress. In 2016, the United Nations declared within their sustainable development goals, affordable and clean energy to be one of its main goals that should be achieved by the year 2030. In the meantime the European Union is targeting a GHG emission reduction of 20% compared to the 1990s and a rise of the renewable energy shares up to 20% of the total European energy consumption within its Europe 2020 strategy (European Commission, n.d.-a). For the period up until 2030, the European climate and energy targets, are even more ambitious.

Even nowadays, nearly one billion people around the globe do not have access to energy (International Energy Agency, 2017). An estimated growth of the global population up to 8.6 billion in 2030 and 9.8 billion in 2050 (United Nations, 2017) will lead to a further increase of the global energy demand and will therefore even intensify the current problem. By 2040, the global energy demand is expected to have increased by around 30 percent, combined with a slight rise of energy related GHG emissions. These circumstances will further exacerbate the issue of environmental pollution (International Energy Agency, 2017b).

Political initiatives trying to reach a sustainable reduction of harmful greenhouse gas emissions call for the following actions:

- an increased share of renewable energy based on the overall energy consumption
- a significant improvement of energy efficiency

While a large variety of powerful renewable energy sources like solar energy, wind, geothermal energy and hydro- or tidal powers can be found all around the globe, most of them suffer from a common disadvantage. Their major drawback is the unsteady energy release, influenced by surrounding conditions like geographic location, season or daytime, not taking into account the real and actual energy demand. If not consumed in the moment of its release or stored for a future use, renewable energy simply gets lost to the environment. Austria for example, is faced with a considerable seasonal electrical energy gap of 11 TWh provided by renewable sources, despite the fact that there is a significant energy surplus in summer (Pauritsch, 2018). Hence, there is an urgent need for technologies able to bridge the time and location gap, between energy provision and actual energy demand. Thermochemical energy storages (TCES) are considered to be a capable bridging technology for thermal energy and will therefore play a significant role concerning an efficient use of renewable energy sources.

The efficiency of solar thermal energy plants would significantly benefit from a combination with TCES due to an extended time of energy generation and enhanced operation conditions. This includes, inter alia, the provision of baseload energy by ensuring the energy generation in times of unsuitable weather conditions (e.g. cloudy, night...) (Gonzalez-Roubaud et al., 2017).

Besides the promotion of renewable energy, TCES could also be a supportive technology for industrial processes, responsible for the majority of energy related CO₂ emissions. Increasing the efficiency of these processes would accordingly reduce the emissions. One possibility would be the usage of industrial excess or waste heat, resulting from residues within production processes, when heat is used in the form of process steam or in fired furnaces. Waste heat, a hitherto largely unused energy source, has the potential to at least satisfy the energy demand of private homes (Miro et al., 2015).

TCES could thereby function as a key technology for harnessing waste heat at a specific temperature level. The International Energy Agency distinguishes between a low (<100 °C), a medium (100 °C – 400 °C) and a high (>400 °C) temperature level (International Energy Agency, 2014). Waste heat could not only be a suitable alternative to non-renewable energy sources, preventing the emergence of new emissions, but further has the potential to meet consumers' energy needs especially in regions without district heating. Additionally, the decoupling of the energy production and the energy demand via TCES would enable the trading of this energy, e.g. on a so-called waste heat exchange. As a result, the economic utilisation would increase the efficiency of the respective processes and simultaneously reduce new energy related emissions. Figure 3 illustrates the European heat demand of different industrial sectors, according to the respective temperature level (Kuder, 2010).

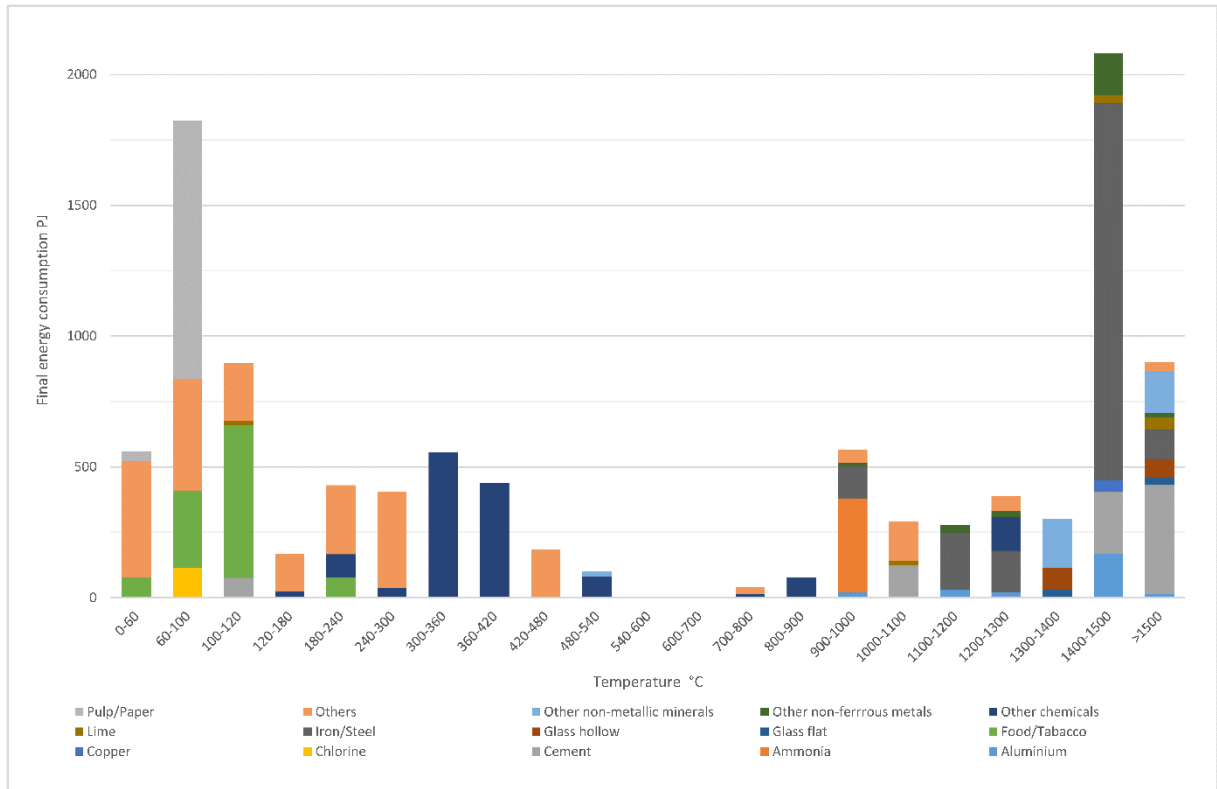


Figure 3 Industrial heat demand for EU-27 (Kuder, 2010)

Finally, the energy crisis of the 1970s and its global consequences, further illustrated the crucial importance of freely accessible and market independent energy sources and resulted in many different political and non-governmental actions. Due to its strong impact on other sustainable development goals, the United Nations therefore defined affordable and clean energy as a major key goal. Storing energy originating from renewable sources via TCES could be one piece of the puzzle regarding a meaningful energy contribution to people (mainly in Asia and Africa), who were hitherto suffering from a lack of thermal or electric energy (United Nations, n.a.-a).

This work therefore focuses on the exploration and development of thermochemical energy storage systems. With more than 50% of the total energy consumption, thermal energy, used for heating, cooking, warming water, industrial processes (process heat, drying and industrial hot water use) etc., constitutes the biggest part of end-used energy and is therefore of existential importance (International Energy Agency, 2019). The vital energy revolution away from fossil energy sources with a vast ecological footprint, towards an energy provision based on renewable energy sources without harmful emissions not only depends on the development of new technologies (like TCES), but also on their success in constituting a considerable share of the overall energy consumption. This work should therefore contribute to a sustainable development, targeting the conservation of this planet and our environment for future generations.

1.2. Objectives

- ❖ Kinetic investigation of two potential thermochemical energy storage systems regarding their chemical suitability for heat storage applications:
 - Representing a high temperature energy storage system: Oxidation process of $\text{Cu}_2\text{O} \rightarrow \text{CuO}$ with respect to the impact of partial pressure, conversion and temperature (Paper III)
 - Representing a low temperature energy storage system: Dehydration process of $\text{H}_3\text{BO}_3 \rightarrow \text{B}_2\text{O}_3$ (Paper I)
- ❖ Macroscopic in-depth analysis of a promising reaction system regarding its suitability as a thermochemical energy storage system
 - Analysis of the reaction system $\text{H}_3\text{BO}_3 \leftrightarrow \text{B}_2\text{O}_3$ (Paper II)

1.3. Sustainable aspects

The aim of this thesis is to analyse the suitability of potential thermochemical storage materials for heat storage. This work therefore contributes to a sustainable future energy provision aspiring to reach a significant decrease of energy related emissions. Thermochemical energy storages are considered to be a promising technology, promoting the exploitation of renewable energy sources by decoupling - and therefore bridging the time gap between - the energy generation and the energy consumption. In addition, by harnessing excess heat this technology can increase the efficiency of processes with waste heat or the energy generation of solar thermal plants, to name just one example. In addition, preventing harmful emissions will contribute to the reduction of the mortality rate, attributed to ambient air pollution.

The objectives of this thesis correspond to the targets of the following political and non-political agreements for climate protection and a sustainable development:

- The Kyoto Protocol
- The Paris Agreement
- The European 2020 Energy Strategy
- The European 2030 Climate & Energy Targets
- UN Sustainable Development Goals
 - Number 3 (SDG 3): Good health and well-being - Ensure healthy lives and promote well-being for all at all ages
 - Number 7 (SDG 7): Affordable and clean energy
 - Number 13 (SDG 13): Climate action- Take urgent action to combat climate change and its impacts

2. Background

2.1. Environmental policy and energy

In the course of history two periods regarding the sustainability of human's energy generation can be differentiated. The "pre-industrial revolution period" was characterised by renewable energy sources like biomass-based ones or occasionally further sources such as wind (in ancient Egypt or China), or hydropower (in the ancient Greek and the Roman Empire). History showed that the cultural growth and upturn mainly depended on the amount of provided energy: the more energy available the faster the respective cultural development.

Furthermore, the conversion of primary energy (like oil, gas, coal, wind, sunshine...), into a consumer-friendly "ready-to-use" form, such as fuel or electricity, as well as the tapping of new energy sources was based on the respective technological progress. The restricted energy provision at this time was a consequence of the respective accessible technical possibilities to harness available energy sources. Thus, mankind's energy demand and the corresponding amount of energy related emissions was consequently limited primarily by the provided amount of energy (Belessiotis and Delyannis, 2000, Keay, 2007).

The "post-industrial revolution period" was characterised by the exploitation of new and mainly non-sustainable energy sources like coal, oil, gas or nuclear fission. The invention of the steam engine in the 18th century was solely responsible for the upward trend of Western European and North American economies. From this moment on, energy was an ubiquitous resource, available whenever and wherever needed. Mankind's hunger for energy gained momentum and so many other energy sources were researched and tapped (Figure 4). As a consequence, energy related emissions exploded (Figure 2) and so did the global pollution, while the impact on the atmosphere remained unnoticed or was mainly ignored.

It was a long way, from the discovery of the greenhouse effect in the 19th century, to the first political response. In 1824, it was the scientist Jean Baptiste Joseph Fourier who for the first time described a global warming effect caused by a veil of gas surrounding the globe - the greenhouse effect (Archer and Pierrehumbert, 2013). His assumption was confirmed shortly after his death by John Tyndall, who in addition recognised that this effect was caused by the gases CO₂, vapour and ozone (Hulme, 2009). In 1896, Svante Arrhenius published the scientific paper, "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground", in which he presented the first precise model calculations and was even able to calculate the temperature rise subject to an increasing CO₂ level (Arrhenius, 1896). It took nearly another hundred years, until the end of the 20th century, for politicians to slowly consider global warming and its harmful impact as a serious global threat.

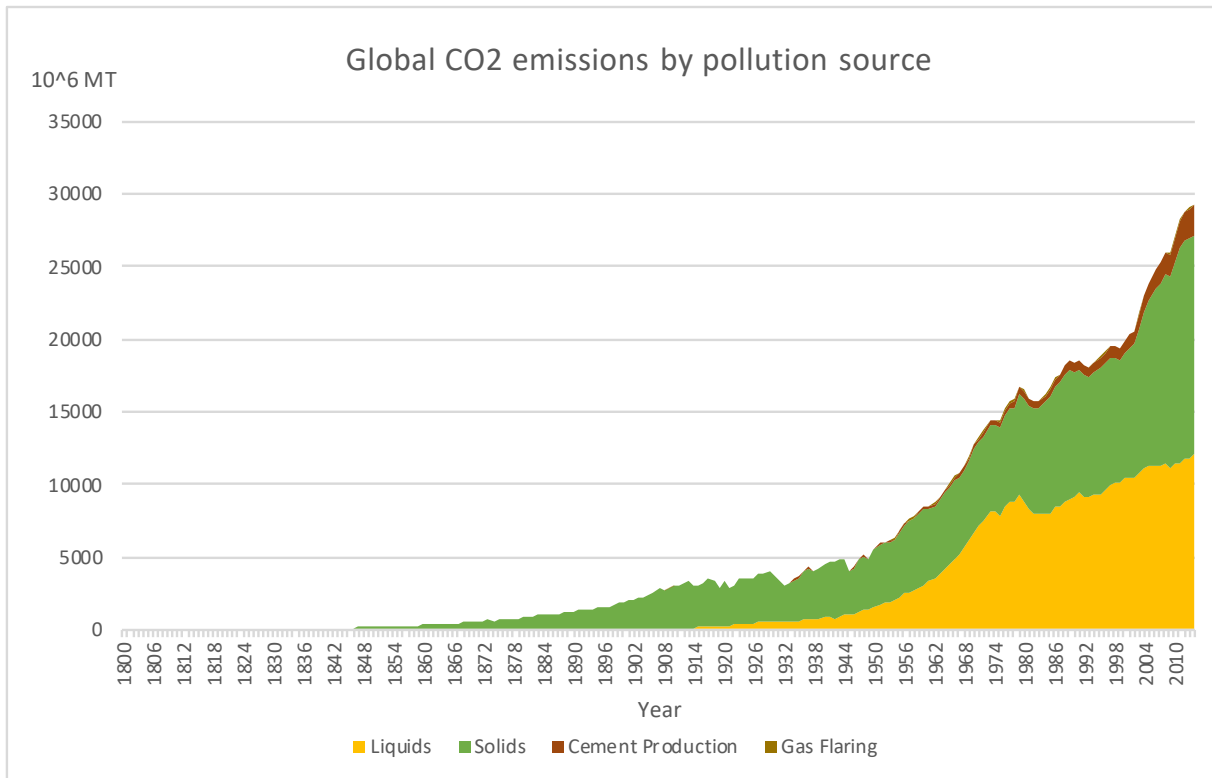


Figure 4 Global CO2 emissions by source from 1800 until 2014 (Boden and Andres, 2017)

Nowadays, it is proven that around thirty different evolving gases like CO₂, CH₄, NO_x or fluorinated gases, are boosting the greenhouse effect. Besides the energy sector, emissions from the agricultural sector (factory farming and grain farming, fertilisers), as well as cement factories, can be counted to be major environmental polluters.

Kyoto Protocol

The Kyoto Protocol concluded in 1997 was one of the first international political agreements concerning environmental protection. It implied a legal obligation, to reduce greenhouse gas (GHG) emissions by 5.2%, compared to 1990 emission-levels by the year 2012. Until a new global agreement will be negotiated, many countries have additionally committed themselves to further emission-cuts, during a second commitment period (2013 – 2020) (UNFCCC, 2018).

Paris agreement

In 2015, at the 21st Conference of the Parties of the United Nations Framework Convention on Climate Change (UNFCCC), a new succession agreement of the Kyoto Protocol fighting climate change was settled. It is the long-term objective of the Paris Agreement to keep the global average temperature rise below 2 °C, compared to pre-industrial times. Ideally the temperature increase should be limited down to 1.5 °C. Each country is obliged to determine, plan and periodically report on its contributions to mitigate global warming (United Nations Framework Convention on Climate Change, 2019).

Europe 2020 strategy

The European Union is further trying to reduce GHG emissions within the scope of the Europe 2020 strategy. The strategy not only targets a reduction of GHG by 20% compared to 1990, but also aims at increasing the share of renewable energy sources up to 20% of the total energy consumption. Furthermore, energy efficiency should rise up to 20% compared to 2005 (European Commission, n.d.-a).

European 2030 climate energy framework

The 2030 climate energy framework further targets a 40% cut of GHG emissions compared to the 90s. Additionally, 27% of the energy consumption should be covered by renewable energy sources, while energy efficiency should likewise increase by at least 27% at EU level (European Commission, n.d.-b). All of these actions identify the use of renewable energy sources and the promotion of efficiency measures as key tasks for a sustainable reduction of GHG emissions.

UN Sustainable Development Goals (SDG)

In 2015 the United Nations adopted 17 global goals, targeting the global development. Every country in the world has accepted these goals, as part of Resolution 70/1 of the United Nations General Assembly. This 2030 Agenda obliges these countries to work towards achieving these 17 goals (Figure 5).



Figure 5 Sustainable development goals (United Nations, n.a.-b)

Regarding the promotion and the increase of the renewable energy share within the global energy consumption, as well as a significant cut of CO₂ emission, sustainable development goal number 7 (SDG 7), “Affordable and Clean Energy”, is of particular importance. About one billion people still have no access to electricity and about three billion are currently suffering from a lack of clean cooking fuels. As a consequence, the resulting indoor air pollution, not only boosts the greenhouse effect, but further constitutes a real threat for people’s health.

Therefore, within SDG 7 the following targets were defined:

- Universal access to modern energy
- Increase the global percentage of renewable energy
- Double the improvement in energy efficiency

Further SDG’s with interdependencies to a clean energy generation and a pollution cut are SDG 13, addressing the stop of climate change and SDG 3 regarding a healthy life (SDG 3).

2.2. Thermal energy storages (TES)

Political demands for climate protection, are calling for a radical CO₂ cut and a sustainable energy provision. Currently, more than 50% of the global consumed energy is dedicated to heat. Thermal energy storages will play a major role towards a clean energy revolution, by meeting the actual energy demand via providing energy from sustainable sources and by increasing energy efficiency.

Independently of the storage mechanism, heat storing cycles typically consist of three steps:

- the charging step (energy is stored into the medium),
- the storage step (stored energy is reserved until it is demanded),
- and the discharging step (energy is released for its usage).

Every thermal storage system, depending on the storage type and the storage material, has a specific energy density and provides the stored energy depending on system- intrinsic properties. Various factors are decisive for the suitability of a respective storage material, depending on the intended application, such as thermo-physical properties (melting point, high latent heat, high specific heat and high thermal conductivity...), availability, price, chemical and thermal stability, low volume change, low vapour pressure, non- toxicity,...(Alva et al., 2017). Up until now, three different thermal energy storage systems are classified, distinguished by their operating principle of storing heat. All of them comprise of different advantages and disadvantages and cover different fields of application:

- sensible heat storage systems,
- latent heat storage systems and
- thermochemical heat storage systems

Table 1 lists respective storage densities and applicable temperature ranges of representative storage materials based on different storage mechanisms.

Sensible heat storage

The oldest and therefore most familiar heat storage principle is based on a sensible heat increase within the storage material – depending on the material’s specific heat capacity - called sensible heat storage. Besides a variety of available storage materials, enabling manifold application temperatures, the storage process of this storage type always follows the same pattern. The storage gets charged via a heating up of the storage material and discharged via a respective temperature decrease. The stored energy (based on the heat absorption during the heating up of the storage material) is proportional to the density, volume, specific heat and temperature variation of the storage material and is defined by

$$Q = m \cdot \int_{T_1}^{T_2} c_p dT$$

where m [kg] is the sample mass, c_p [kJ/kg K] the sample material’s specific heat capacity, T_1 [K] the surrounding temperature and T_2 [K] the temperature of the heat storage. Figure 6 illustrates the storage principle. The operating principle of sensible energy storages is restricted to the sensible heat excluding phase change (Alva et al., 2018). The physical limits of this storage type are defined by the properties of the material, the maximum storage-temperature for example, is restricted by the phase transition temperature. Important criteria for sensible heat storage materials are inter alia a high specific heat capacity, an easy availability, environmental friendliness (non-toxicity), as well as a suitable temperature range for the stored heat. The prevalent storing material for sensible heat below 100 °C is water, because it is best suitable for household applications such as heating, hot water supply or cold food storage. Higher temperatures require the usage of other materials like sand, thermal oils (up to 400 °C) or salts (up to 600 °C) (Alva et al., 2017). The limited storage time, a result of the huge energy loss during the storage period, is caused by the function principle of storing energy at a higher temperature level, compared to the surrounding. To handle this big disadvantage of this storage type, a proper insulation is always required. For high temperature applications, sensible heat storages are currently the most used thermal energy storage systems. Table 1 lists suitable sensible storage materials.

Latent heat storage

Already, for a while, a second type of heat storage system – the latent heat storage system – has attracted scientific attention. Compared to specific heat, the latent heat of materials is 50-100 times bigger and the energy density of latent heat storage systems respectively higher (Alva et al., 2018). At the present time, the first commercial storage systems based on this technology, are now available on the market.

The characteristic element of this storage system, is the phase change process of the storage material, therefore also called phase change materials (PCM). The stored energy is the latent heat of the phase change at a constant temperature (phase change temperature). Different phase change processes like solid-solid, solid- liquid and liquid- gaseous are available. The liquid- gaseous phase change has the highest latent heat of phase change (Cárdenas and León, 2013). Nevertheless, the high-volume change during the storage process causes technical problems which is why this phase change is quite unpopular (Alva et al., 2018).

The energy storage content of a latent heat storage system is defined by

$$Q = m \cdot \left(\int_{T_1}^{T_{PC}} c_{p1} dT + \Delta H_{PC} + \int_{T_{PC}}^{T_2} c_{p2} dT \right)$$

where m [kg] is the storage materials mass, c_{p1} [kJ/kg·K] and c_{p2} [kJ/kg·K] the specific heat capacities before and after the phase change, T_1 [K] the surrounding temperature, T_{PC} [K] the phase change temperature, T_2 [K] the final temperature after the charging process and ΔH_{PC} [kJ/kg] is the energy of the phase change.

This equation is considered to illustrate the sequence of two sensible heating up steps (from the surrounding temperature to the phase change temperature and from this temperature to the end temperature of the heat source) and the phase change step (at constant temperature) in between (Figure 6). The phase change enthalpy, as well as the phase change temperature, are the main criteria for the suitability of storage materials. Table 1 lists suitable latent heat storage materials.

A disadvantage of latent energy storages is their limited storage time. During the storage period, a huge amount of energy gets lost, due to the fact, that storing energy at a higher level, compared to the surrounding always leads to an unstoppable energy loss. This is why a proper insulation is required. Depending on the intended operating storage cycle temperature and the intrinsic phase change temperature of the storage material, various materials are used for latent heat storages, such as organic compounds (paraffin, fatty acids, esters, alcohols...) or inorganic compounds (salts, salt eutectics, salt hydrates...).

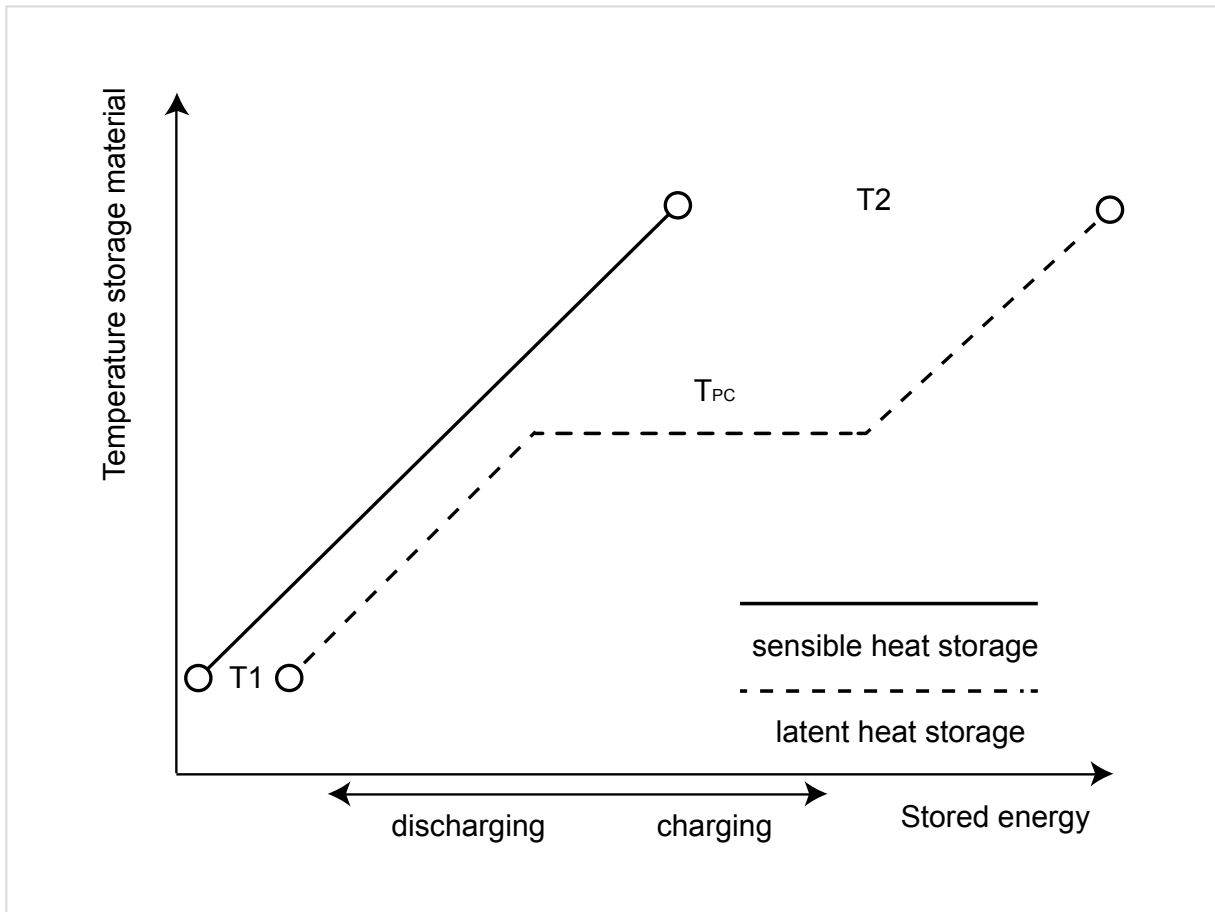
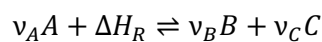


Figure 6 Storage principle - sensible versus latent heat storage

Thermochemical energy storage (TCES)

Thermochemical energy storage (TCES) systems are still at a research stage, but due to their much higher energy density, compared to sensible and latent heat storages, they receive steadily increasing scientific attention. In contrast to sensible and latent heat storages, the function principle of TCES systems is based on a storage material change during the storage process. TCES systems utilise the reaction enthalpy of reversible chemical reactions. The reaction sequence thereby consists of the following steps: charging, storing and discharging. During the energy storing process, supplied heat gets absorbed and thereby the initial product A decomposes into two products B and C (Figure 7). The resulting products contain the reaction enthalpy of the first step and are ready for storage. By turning B and C finally back into A, the stored energy will be released in form of an exothermal reaction and makes the reaction heat available for consumption (Figure 7).



To simplify the product separation before storage, the two obtained products B and C should ideally differ in their physical state, preferably with one gaseous product. If the volatile product C is easily

available and cheap, the storage volume could be significantly reduced by storing only the non-gaseous product B.

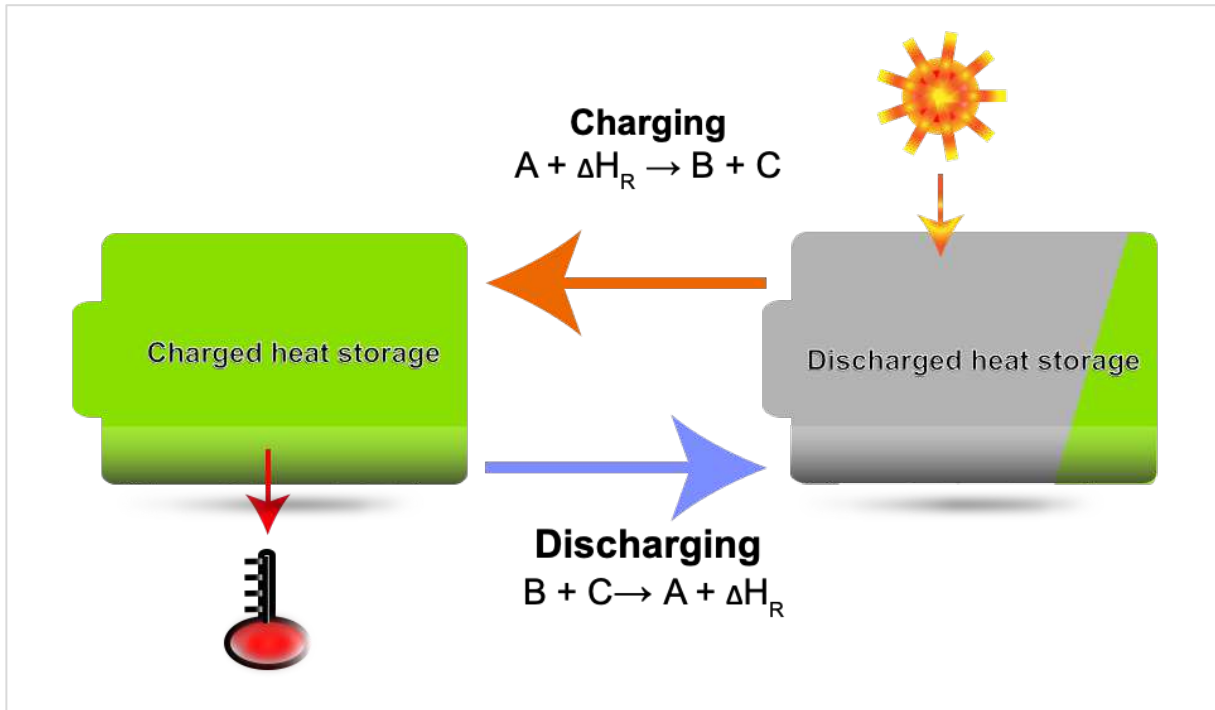


Figure 7 Storage principle - thermochemical heat storage

The reaction's path is controlled (according to the Gibb's free energy) by temperature and pressure. For standard pressure, the transition temperature T^* can be determined via the thermodynamic equilibrium condition for change in Gibb's free energy ΔG as zero

$$\Delta G(T^*) = 0$$

$$\Delta G(T^*) = \Delta H(T^*) - \Delta S(T^*) \cdot T^*$$

$$T^* = \frac{\Delta H(T^*)}{\Delta S(T^*)}$$

where ΔG is the Gibb's energy, ΔH the enthalpy and T^* the transition temperature. For $T > T^*$ the decomposition reaction is prevalent and for $T < T^*$ the reaction of formation.

Despite having the highest energy storage density, thermochemical energy storages are determined by technically challenging processes with a variety of influencing factors on the storage suitability. Sintering effects during the decomposition, for example, could cause grain growth and lead to a lower porosity, which in turn hampers the reaction of the formation. In general, potential effects with a strong impact on the cycle stability and the reaction kinetics of the storage process, are crucial for a commercial application of this technology and therefore need to be well investigated in order to avoid later occurrences (Alva et al., 2018). Table 1 lists TCES that work well.

Table 1 Comparison of different thermal energy storage systems (TES)

Type	Material	Energy storage density	Temp-range/ Melting point	Ref.
Physisorption TES	Zeolites 13X/H ₂ O	601 MJ/m ³	65 - 130 °C	(Cabeza et al., 2017)
Chemisorption TES	MgSO ₄ x 7H ₂ O	1512 MJ/m ³	150 °C	(Cabeza et al., 2017)
Sensible TES	HITEC solar salt	2.9 MJ/m ³	250 – 450 °C	(Gonzalez-Roubaud et al.,
Sensible TES	H ₂ O at 50 °C	206 MJ/m ³	50 °C	(VDI-wärmeatlas,
Latent TES	MgCl ₂	1048 MJ/m ³	714 °C	(Zalba et al., 2003)
Latent TES	NaF	2031 MJ/m ³	996 °C	(Alva et al., 2017)
TCES	Cu ₂ O	3606 MJ/m ³	350 - 1100 °C	(Setoodeh Jahromy et al., 2019)
TCES	H ₃ BO ₃	2238 MJ/m ³	90 - <200 °C	(Roine, 2007)

3. Methodology

3.1. Identification of potential reactions

The identification of potential thermochemical energy-storage reactions, was developed in-house and resorted to a systematic search algorithm, (Deutsch et al., 2016). This algorithm was designed to find possible solid/ gas reactions for a specified set of materials. Applied to a chemical database, all possible decomposition reactions, fulfilling the boundary conditions (limited number of stoichiometric coefficients), were restricted to reactions of solid inorganic substances with a defined gaseous reactant. A further reduction of the more than thousand resulting reactions was achieved by limiting the equilibrium temperature to 1000 °C and by other limitations associated to the heat storage capacity, availability and material costs. In a first step, the resulting potential reactions were briefly analysed via different analytical techniques to prove their suitability and were then ranked regarding their characteristics. As a result, boric oxide and copper oxide were analysed in-depth.

3.2. Sample Material

For the analyses, sample material was taken from:

- Paper III
 - Copper oxide: Merkur Emsure
- Paper I
 - Boric acid: Sigma Aldrich (11606/CAS: 10043-35-3)
 - Boron oxide: Alfa Aesar (12290/ CAS: 1303-86-2)
 - Metaboric acid: Santa Cruz Biotechnology (sc-228460/ CAS: 13460-50-9)
- Paper II
 - Boric acid: Carl Roth GmbH (6943/ CAS: 475234072)

3.3. Sample preparation

Before being analysed the respective samples were prepared as follows:

- Paper III
 - grinding using a planetary ball mill (Retsch PM 100)
 - sieving
 - limiting the particle size for the analyses from 1 to 100 μm
- Paper I
 - Grinding in parts using a planetary ball mill (Retsch PM 100)
 - Particle size analysis using a laser diffraction measurement device (Mastersizer 2000, Malvern Instruments)
- Paper II
 - Particle size analysis using a laser diffraction measurement device (Mastersizer 2000, Malvern Instruments)

3.4. Experimental set-up & analysis methods

Thermal Analysis

Within this work thermal stimulated processes were analysed. The experimental gravimetric analysis was therefore performed via a simultaneous thermal analysis device (Netzsch STA 449 Jupiter and equipped with a TGA-DSC sample holder). For all the experiments, aluminium crucibles ($\phi= 6 \text{ mm}$, $V=75 \mu\text{l}$) were used without lids. The instrumental characteristics enabled sample examinations under thermal exposure, ranging from 25 to 1250 $^{\circ}\text{C}$ and regulated by an S-Type thermocouple for isotherm and dynamic (with constant heating-rate) analyses. The gas flows (oxygen and nitrogen) were regulated via mass flow meters (Red-y smart, Voegtin). The flow rate of nitrogen was set to 100 ml/min prior to each experimental run. To remove residues of oxygen before each oxidation experiment, the reactor with the sample was purged with nitrogen for at least 30 minutes. The device was capable of being equipped with a steam generator, also enabling thermal investigations under defined moist conditions.

The analysis of the copper oxide oxidation reaction (Paper III) was performed under isothermal conditions and various oxygen partial pressures (1.0, 0.5, 0.2 and 0.1 bar). For the boric acid decomposition reaction (Paper I and Paper II), the analysis was performed under dynamic (non-isothermal) conditions, with heating rates of 2, 4 and 8 $^{\circ}\text{C}/\text{min}$.

For the experimental analyses, it was important that the experimental realisation was compliant with recommendations of the Kinetics Committee of the International Confederation for Thermal Analysis

and Calorimetry (ICTAC). During the set of thermal analyses, the sample mass was kept practically constant. Other major factors with impact on the quality of the analysis – such as the gas atmosphere or heating rate (Paper I and Paper II) - were controlled. For the dynamic experiments (Paper I and Paper II), the heat was therefore the only theoretically remaining variable. The fine powder samples were spread as a thin layer on the pan bottom, to ensure a homogeneous reaction progress of the samples without mass influence on the reaction rate. In addition, for a dynamic analysis of decomposition reactions (Paper I and Paper II), moderate reaction rates and a sufficient inert gas flow for an immediate gaseous product removal were suggested. Fast heating rates should be generally avoided, as they enhance the temperature gradient in the sample particles and thus cause a non-uniform reaction with negative influence on the reliability of the experimental data.

Enhanced Deconvolution procedure

The kinetic evaluation is based on measured variables (properties such as mass or evolved or consumed reaction heat), as the sample is heated up (dynamic experiments) or held at a constant temperature (isothermal experiments) (Khawam, 2007). This measured variable is directly related to the individual reaction α . Common analysis-methods are hitherto not applicable on reactions consisting of multiple reaction steps. For reactions with several overlapping rate peaks, it is therefore indispensable to separate the overall (sum) measured reaction data into single reactions, thus enabling the individual kinetic analysis.

For the separation of overlapping independent steps, a new procedure, based on a mathematical deconvolution of the overall rate peaks was performed. First proposed by Perejon et al. (2011), the overlapping rate peaks were separated, using various mathematical peak functions, which revealed the individual steps. After this procedure the individual rate peaks were analysed via an isoconversional kinetic analysis method, yielding the respective kinetic triplets. Currently, this procedure has become increasingly popular for kinetic analysis of various processes (Vyazovkin et al., 2018).

The findings of Perejon et al. (2011) showed the suitability of asymmetric peak fitting functions. The Fraser-Suzuki function was considered to be the most appropriate, due to its capability of fitting a function (asymmetric and symmetric) properly and independently of the kinetic model. Since rate peaks are often asymmetric, symmetric peak functions are usually not recommended (Vyazovkin et al., 2018). The use of the Fraser-Suzuki function enables correct parameters of subsequent kinetic analysis even if the reaction results deviate from the kinetic model due to inhomogeneities (a frequent problem of heterogeneous reactions).

The Fraser-Suzuki function is defined as (Svoboda and Málek, 2012):

$$y = a_0 \exp \left[-\ln 2 \left[\frac{\ln \left(1 + 2a_3 \frac{x-a_1}{a_2} \right)}{a_3} \right]^2 \right] \quad (1)$$

With the parameters a_0 , a_1 , a_2 and a_3 for the amplitude, position, half-width and asymmetry of the peak.

In addition, for the application of the deconvolution within Paper I this procedure was enhanced by stoichiometric information, since the deconvolution is exclusively a mathematical process. This means, to be accepted the resulting shares of the individual rate peaks had to correspond to the shares of the respective stoichiometric mass loss. This condition also ensured the chemical justification of the mathematical results.

Kinetic fundamentals

The General Kinetic equation is a parameterisation of the process rate and consists of three variables: the Temperature T , the extent of conversion α and the pressure P (Vyazovkin et al., 2011). For a heterogeneous reaction the reaction rate is defined as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (2)$$

with the temperature dependence $k(T)$, the reaction model $f(\alpha)$ and the pressure dependence $h(P)$.

Reaction models are theoretical descriptions of experimental results, describing different reaction types and mechanisms based on mechanistic assumptions or empirical derivations. Up until now, the pressure dependency $h(P)$ is largely neglected, even though it can possibly influence the kinetics of reactions with a gaseous reactant and/or product. For oxidation and reduction reactions for example, the reaction kinetics strongly depends on the partial pressure of the gaseous oxidant or reductant. There are different options to describe the pressure dependency, depending on the reaction conditions (e.g. power law for autocatalysis).

The temperature dependence $k(T)$ inter alia can be modelled via the Arrhenius equation:

$$k(T) = Ae^{(-\frac{E_a}{RT})} \quad (3)$$

with the frequency factor A, the absolute Temperature T and the activation energy E_a .

Many papers dealing with reaction kinetics call $f(\alpha)$, A and E_a the kinetic triplet. Consequently, the kinetic triplet is mainly provided as an essential finding of the kinetic analysis.

For a gravimetric measurement the extent of reaction is defined as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (4)$$

with m_0 as the initial mass, m_t as the mass at time t and m_∞ as the final weight.

For dynamic experiments the heating rate β can be implemented, yielding the non-isothermal rate expression:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) f(\alpha) h(P) \quad (5)$$

Kinetic identification NPK with respect to pressure impact

Kinetic analysis methods can be distinguished in model-fitting (pre-assuming a model) and model-free methods. Within this thesis a model-free method, called the non-parametric method (NPK) was used for the kinetic modelling. This method was first proposed in 1998 by Serra et al. (1998) and further refined in-house (Deutsch et al., 2017a, Birkelbach et al., 2019). It is based on the observation, that the discretisation of the General Kinetic Equation (2) results in a rank-one matrix. By arranging the experimental reaction data in a matrix and using an appropriate algorithm to compute its rank-1 approximation, it allows the extraction of different variables (conversion, temperature dependency and pressure dependency), without any prior model assumption besides the single step approximation.

Models are selected and parametrised after the separation of the variables, independently of each variable (T, α and P) via fitting the resulting vector. The calculated uncertainty of each resulting vector was weighted accordingly and should guarantee the quality of the model fitting step. The best fitting reaction model for the respective reaction data, was discovered by fitting 41 reaction models (from literature) to the calculated conversion dependency vector.

Macroscopic reaction heat analysis

It was impossible to analyse the forming boric acid reaction via thermal analysis due to the evaporation of formed boric acid in the presence of water. The application of a simple Dewar reactor finally enabled an accurate analysis of the macroscopic hydration reaction (Figure 8). This reactor comprised a Dewar vessel with a capacity of one litre, a stirrer and a thermocouple with a logging function. The high hygroscopic behaviour of boron oxide called for a water surplus to ensure a good mixing quality and a homogeneous reaction progress.

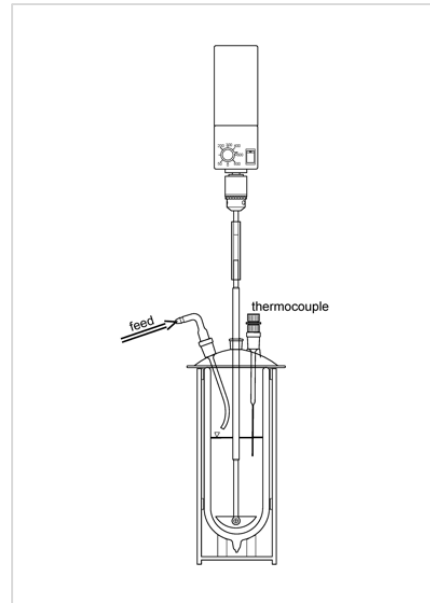


Figure 8 Dewar reactor

X-ray diffraction

For the analysis of the sample structures in all papers, an X-ray diffraction analysis device (XRD) was used. The different measurements were performed on a PANalytical X'Pert diffractometer device in Bragg-Brentano geometry. It is equipped with a mirror for separating the Cu $K\alpha_{1,2}$ radiation and an X'Celerator linear detector with Ni Filter. The Anton Paar HTH1200N chamber enabled an in-situ monitoring of the experiments and the diffractograms were evaluated with HighScorePlus (PANalytical).

Scanning Electron Microscopy (SEM)

For a deeper insight into the sample structure, SEM analyses were performed. For imaging the samples surface morphology two different devices were used:

- Paper III & Paper II: FEI Quanta 200 FEG SEM, equipped with a Schottky emitter, it enables an operating range of 200 V to 30 kV with an Everhart-Thornley Detector for secondary electrons in action.
- Paper I: Coxem EM-30 Plus, equipped with a Tungsten Filament emitter, it enables an operating range between 1 and 30 kV

Brunauer-Emmett-Teller (BET) analysis

For the physisorption measurements an ASAP 2020 (Micromeritics) device was used. At the beginning of the analysis, the sample was heated up to 120 °C under vacuum for several hours to eliminate adsorbed gases and moisture. For boric acid and boron oxide, this analysis method was not applicable. During the prior heating up under vacuum, the surface changed due to fusion and the material densified, having significant impact on the real material characteristics. A BET analysis is therefore inappropriate for these materials.

Particle Size Distribution analysis

For the analysis of the particle size, a laser diffraction measurement device, Mastersizer 2000 (Malvern Instruments) was used. The particle-in-gas sizing was enabled by the dry dispersion module Scirocco 2000, using water as dispersion fluid, thus providing a particle size analysis in the interval of 0.02 to 2000 μm .

4. Kinetic investigation on two selected potential thermochemical energy storage systems regarding their chemical suitability for heat storage applications:

This chapter is dedicated to the kinetics of promising energy storage reactions with a high energy density. It comprises the research findings of two different reactions, which enable the storage of thermal energy at a high and a low temperature level. The following two papers illustrate the reaction's kinetic model, suitably describing the reaction progress and thus enabling a large-scale reactor design.

4.1. Paper III: Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu_2O to CuO in Thermochemical Energy Storage.

Copper oxide is considered as a suitable reaction material for the storage of thermal energy at a high temperature level. Compared to other potential reactions, copper oxide has a high energy density (Table 1). Previously, various kinetic analyses of this reactions system were performed, though all of them struggled with the mathematical description of the influence of the oxygen partial pressure on the reaction kinetics. The kinetic of heterogeneous gas-solid reactions, in particular for reactions with a gaseous component, are significantly affected by the prevailing pressure. A former work by Deutsch et al. (2017b) reported a negative activation energy for the decomposition reaction of CuO to Cu_2O . To extrapolate the reason for this phenomenon, an in-depth analysis of the pressure term in the general kinetics equation was necessary. This paper was therefore, for the first time dealing with the evaluation of the oxygen partial pressure influence on the reaction kinetics of the copper oxide oxidation reaction as shown in Figure 9. Isothermal analyses, using the STA device, were performed at temperatures between 800 °C and 930 °C with different oxygen partial pressures (0.1, 0.2, 0.5 and 1.0 bar). In addition, the sample characteristics were analysed via XRD, BET and SEM.

Results and discussion

The ideal investigation conditions (e.g. mass, partial oxygen pressure) for the reaction were defined by preliminary experiments and ensured the good quality of the analysis. The evaluated experimental equilibrium progression of the oxygen partial pressure was experimentally confirmed and perfectly corresponded to the literature data (Figure 10). Furthermore, for the isothermal experimental run at a temperature of 930 °C, a good conversion higher than 94 wt% was reached (Figure 11). The experimentally evaluated specific energy storage densities of the oxidation and reduction reaction thereby were corresponding to each other. Table 2 lists the evaluated specific energy content of oxidation and reduction at a reaction temperature of 930 °C. The experimental conditions were responsible for a significant deviation from the theoretical specific energy contents for CuO . The loss of energy was a consequence of using crucibles without lids for the thermal analysis, thus accepting a

not measurable energy loss to the surrounding. Figure 12 illustrates the kinetic parameters for the isothermal analysis at 800 °C and 830 °C and revealed that the reaction can be most suitably described via nucleation models (A2, A5). Nucleation models, characterising different nucleation types and crystal dimensionalities, are frequently used to describe various solid-state reactions (e.g. decomposition, adsorption, hydration, desolvation...). Solid state crystals offer, due to deviations from the ideal state (like impurities, cracks, edges or other) many reactive sites with a minimised local activation energy. At these positions, in the lattice of Cu₂O, new phases of CuO can start to form easily. Figure 12 illustrates the evaluated parameter progression of the kinetic analysis for the overall experimental dataset. The A2 model was best describing the reaction data (highest regression coefficient), yielding an activation energy of 76.7 kJ/mol. The evaluation revealed the temperature trend cannot be described by the Arrhenius equation. To address this issue, there was need for some improvements in the evaluation. The consideration of the pressure influence on the kinetic results, via reparameterisation of the pressure parameter to $(1-P/P^*)^n$ produced relief. It enabled the general equation taking the distance to the equilibrium curve into consideration. The reparametrised parameters are represented by Figure 13. The results for the temperature term showed a high temperature dependence on the Arrhenius equation. The pressure term, presenting the impact to the kinetics, was evaluated subject to the distance to the equilibrium oxygen partial pressure. The closer the oxygen partial pressure is getting to the equilibrium partial pressure, the lower the influence of the pressure on the kinetics, completely vanishing at the equilibrium partial pressure level. The best fitting reaction model to the experimental data was still the nucleation model A2, with an activation energy of 233 kJ/mol and a frequency factor of 5×10^9 1/s.

The general equation for the oxidation reaction under consideration of the oxygen partial pressure can therefore be written as:

$$\frac{d\alpha}{dt} = 5 \times 10^9 \times e^{(-233000/RT)} \times 2(1 - \alpha)[- \ln(1 - \alpha)]^{0.5} \times a \left(1 - \frac{P}{P^*}\right)^{0.658} \quad (6)$$

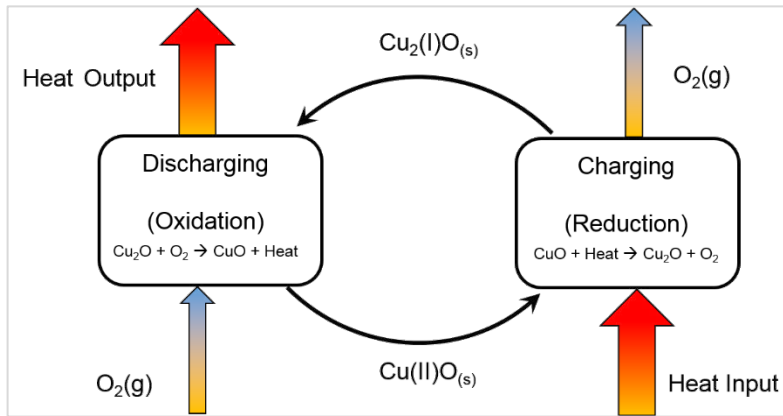


Figure 9 Reaction system for $\text{Cu}_2\text{O}/\text{CuO}$

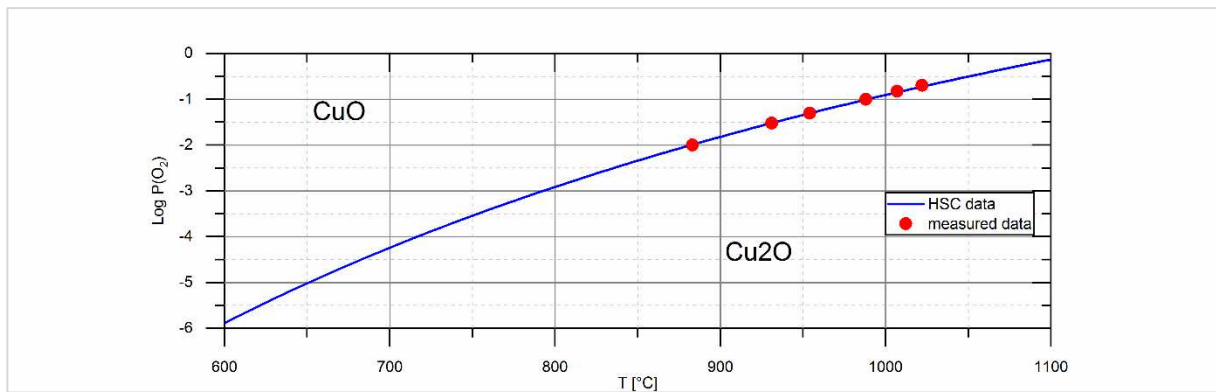


Figure 10 Equilibrium oxygen partial pressure (HSC data vs measured data)

Table 2 Specific energy content in kJ/kg at 930 °C for the CuO reduction and Cu2O oxidation at the respective partial pressure [bar]

Energy content kJ/kg	1. Cycle	2. Cycle	3. cycle	4. cycle
Charging (Reduction, N_2 atmosphere)	525	522	521	523
Discharging (Oxidation)	601	539	508	505
p_{O_2}	1.0	0.5	0.2	0.1

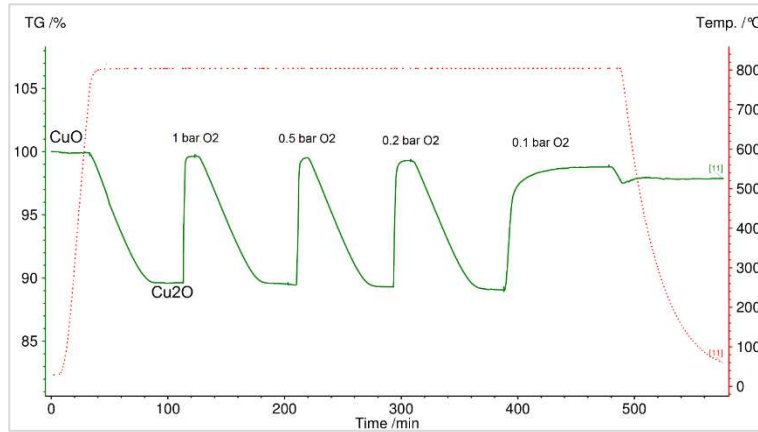


Figure 11 Thermogravimetric analysis (green line) under isothermal conditions at 800 °C (red line) and different oxygen partial pressures (1, 0.5, 0.2, 0.1 bar)

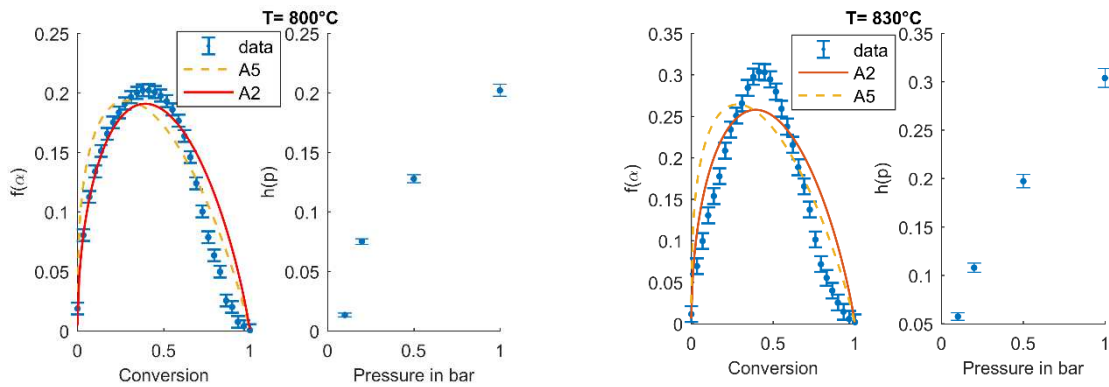


Figure 12 Kinetic models fitting best to the experimental data and the respective pressure influence at 800 °C (left) and 830 °C (right)

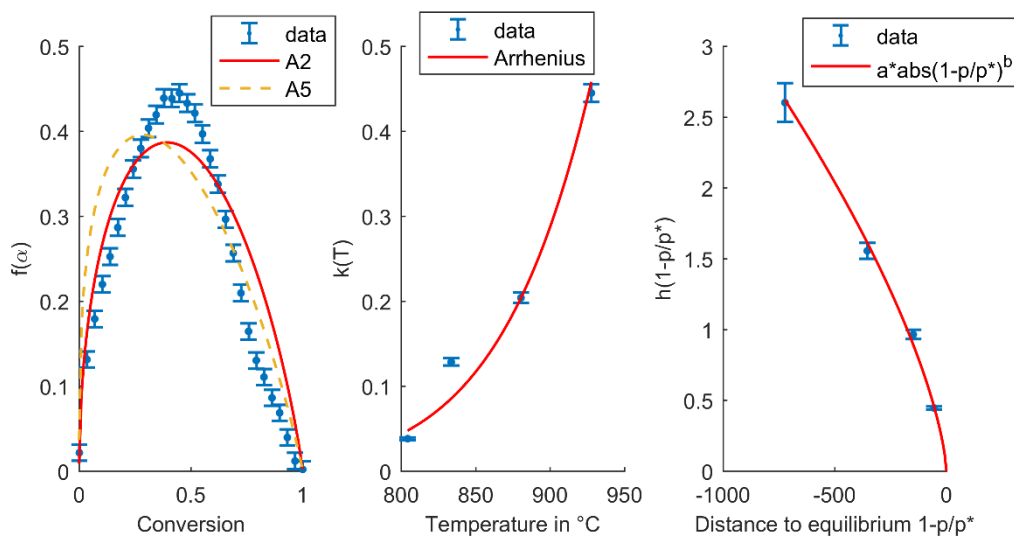


Figure 13 Kinetic parameters after reparameterization of the pressure parameter

4.2. Paper I: The multistep decomposition of boric acid

Boric acid is an highly important resource for various industrial and medical applications. Recently the reaction was also discovered to be an extremely promising thermal energy storage. Up until now, different research teams therefore tried to analyse the decomposition kinetics (dehydration) of this reaction. Unfortunately, two different decomposition mechanisms (2 and 3 reaction steps) are coexisting and the presented analyses results showed a wide range of kinetic parameters. For the desired application of process modelling and reactor design for a thermochemical storage process, reliable kinetic data are essential. One possible reason for the variety in results and the disagreement on the number of reaction steps could be the complex decomposition reaction with overlapping reaction steps. This paper therefore addresses this particular issue for the first time. The methodology combines the separation of the overall reaction data into its single steps via the deconvolution and the subsequent kinetic analysis of each reaction step using the NPK2 method (Figure 14).

Results and discussion

For the boric acid decomposition analysis experimental thermogravimetric data with constant heating rates of 2,4 and 8 °C/min were used (Figure 15). The data of the overall reaction were separated into the respective numbers of steps (2 and 3) by the deconvolution procedure, according to the proposed reaction mechanisms in literature (number of reaction steps). The resulting steps were then compared to the respective stoichiometric mass loss to ensure the ratios to be coherent. For a 2-step reaction the yielded ratio of the single step reaction rates (Figure 16) was neither able to show a good correlation, nor was it matching to the respective stoichiometric ratio of 67:32 % (Figure 17). However, the results of the 3-step reaction deconvolution showed a good correlation to the experimental data. Furthermore, the resulting single reaction rate ratio was matching well, to the stoichiometric ratio of 66:17:17 %. (Figure 18). The 3-step reaction mechanism was therefore considered more suitable to describe the decomposition reaction and thus was used for the kinetic analysis. The respective conversion and conversion rate was calculated for each reaction step and is shown for step 1 in Figure 22, step 2 in Figure 23 and step 3 in Figure 24. The evaluation of the kinetic parameters via the NPK method yielded the reaction model and the temperature dependence. The first reaction step matches best to a reaction order model (Figure 22). The baseline caused blurs at the beginning and thereby prevented a clearer identification of the result. A nucleation model statistically fits best to the second reaction step (Figure 23). The data of the last step indicates the third step to follow a diffusion-derived model (Figure 24). The temperature dependency of all reactions followed the Arrhenius equation. The resulting kinetic parameters are presented in Table 3.

Furthermore, the results revealed structural changes during the reaction. The occurrence for this melting or formation of amorphous phases below the melting point calls for further analysis works on the decomposition under thermal exposure.

This work's results intend to support the reactor design for thermal energy storage systems. It was revealed that the deconvolution can be a supportive technique for the analysis of multistep reactions with overlapping rate peaks. For this procedure's chemical justification, it is advisable to check whether the results chemically correspond to the reaction (e.g. stoichiometry, number of steps...). The decomposition reaction of boron oxide is hard to analyse, because of boron's complex characteristics causing a scientific disagreement about the right reaction mechanism and the number of steps. The formation of amorphous phases and the reason for this, is a still an unsolved phenomenon. This work's methodology therefore facilitates a new view on this particular reaction and the results will further elucidate the decomposition reaction by the provided results.

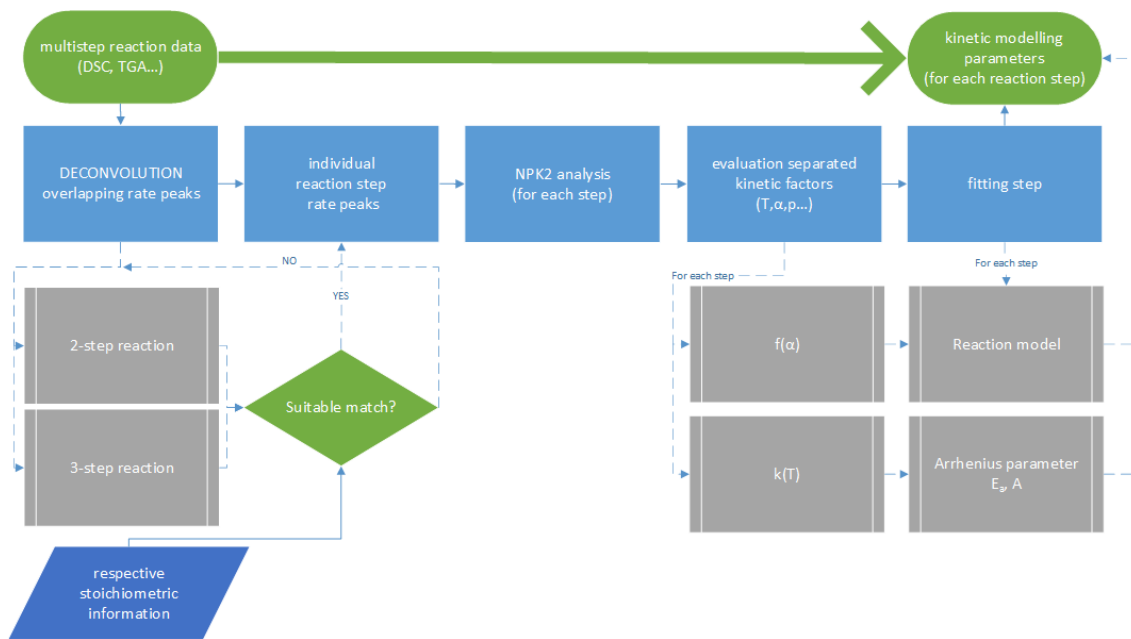


Figure 14 Methodology of combining the deconvolution with the subsequent kinetic analysis of overlapping reaction rate peaks

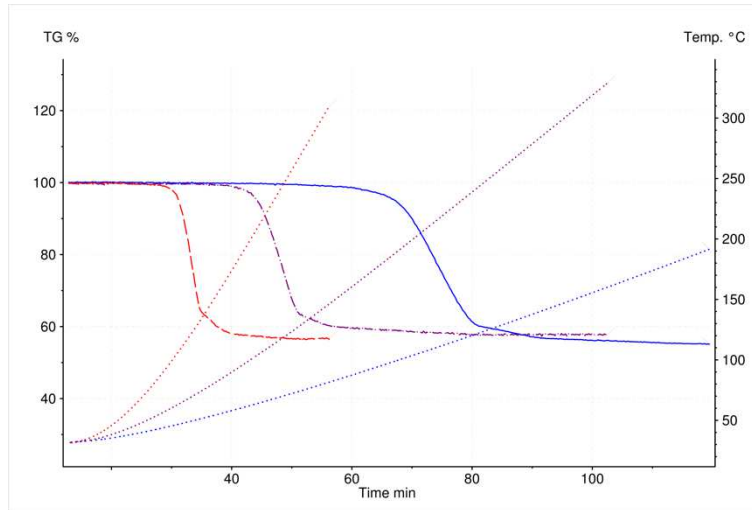


Figure 15 Decomposition of boric acid- thermogravimetric data at heating rates of 2 4 and 8 °C/min

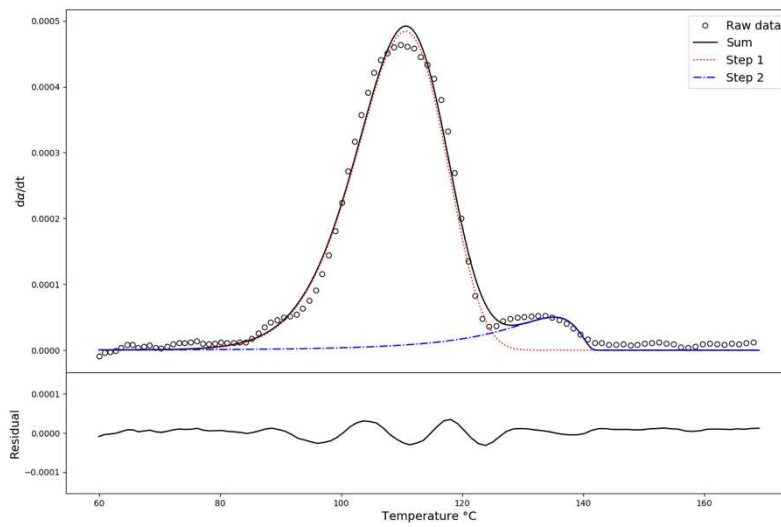


Figure 16 Deconvolution for a 2-step mechanism at a heating rate of 2 °C/min giving a 91:9 % ratio of the steps

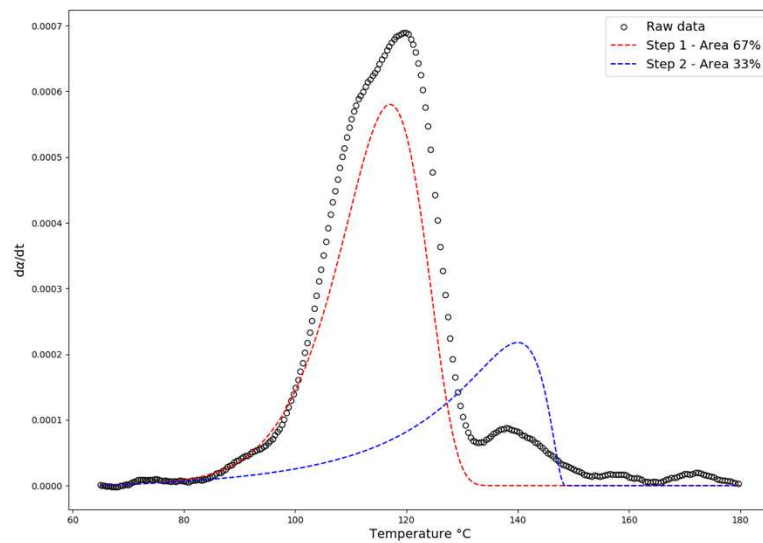


Figure 17 Experimental reaction data versus 2-step stoichiometric ratio of 67:33 % for experimental data at a heating rate of 4 °C/min

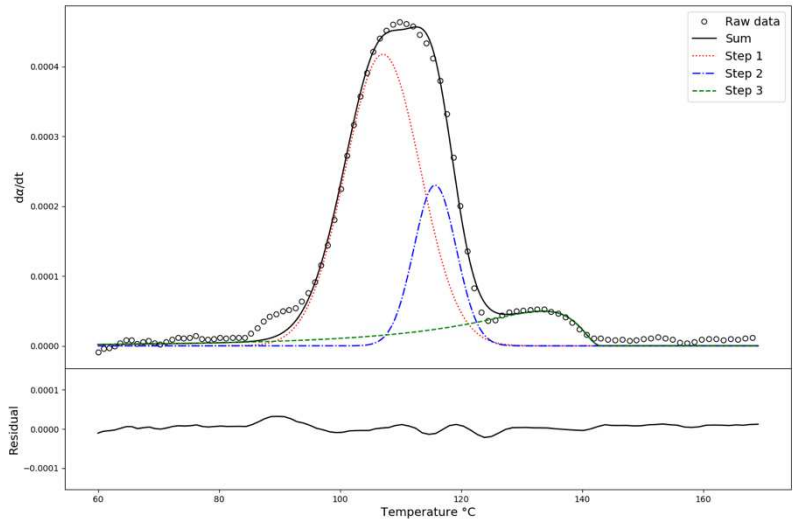


Figure 18 3-step deconvolution applied on experimental data at a heating rate of 2 °C/min

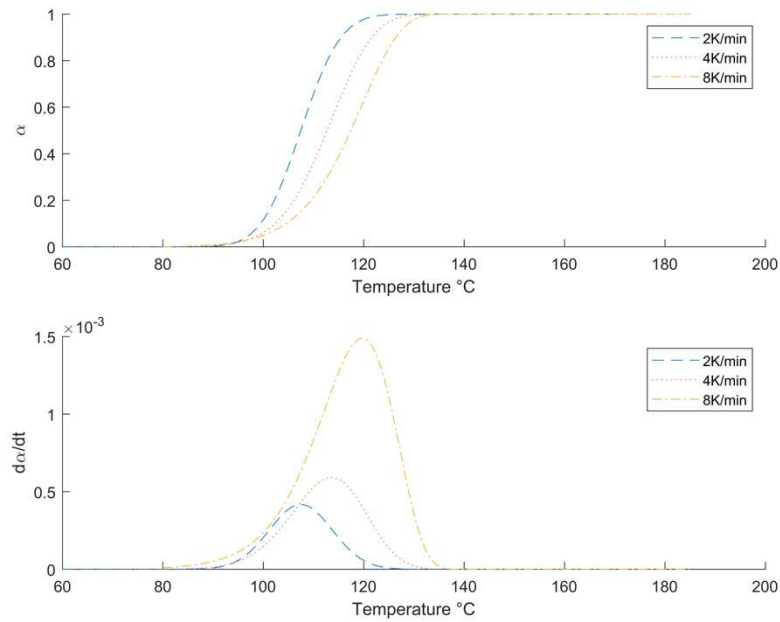


Figure 19 Conversion and conversion rate calculated for reaction step 1

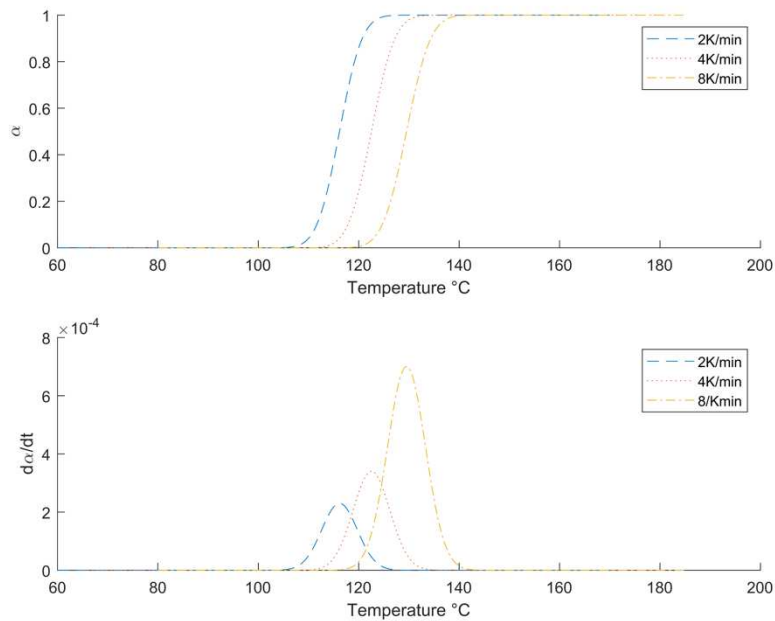


Figure 20 Conversion and conversion rate calculated for reaction step 2

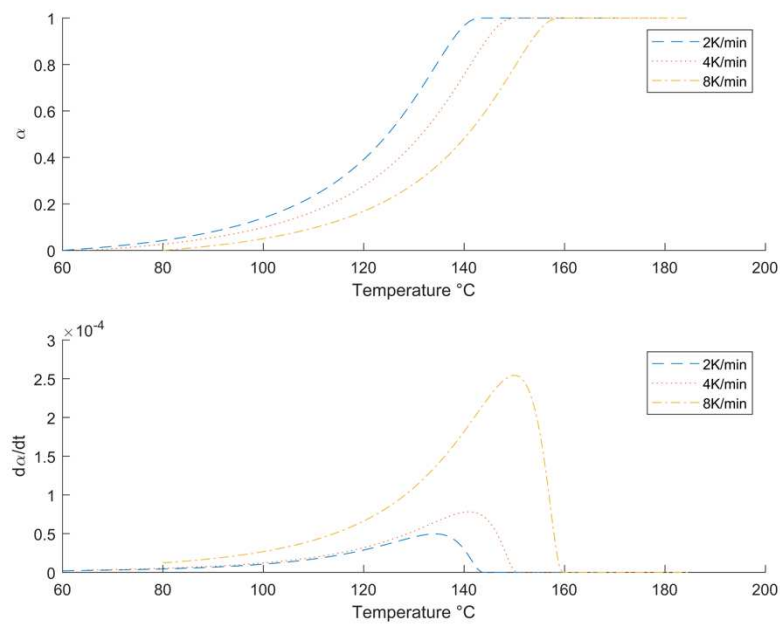


Figure 21 Conversion and conversion rate calculated for reaction step 3

Table 3 Kinetic results for each reaction step

reaction step	reaction path	model	A [1/s]	E _a [kJ/mol]	95% confidence interval of E [kJ/mol]
1	H ₃ BO ₃ > HBO ₂	Fn 5/4	2.3·10 ²³	193.3	(189.6, 197.0)
2	HBO ₂ > H ₂ B ₄ O ₇	A2	1.4·10 ¹²	117.6	(113.3, 121.9)
3	H ₂ B ₄ O ₇ > B ₂ O ₃	D2	9.4·10 ¹⁴	149.6	(148.0, 151.2)

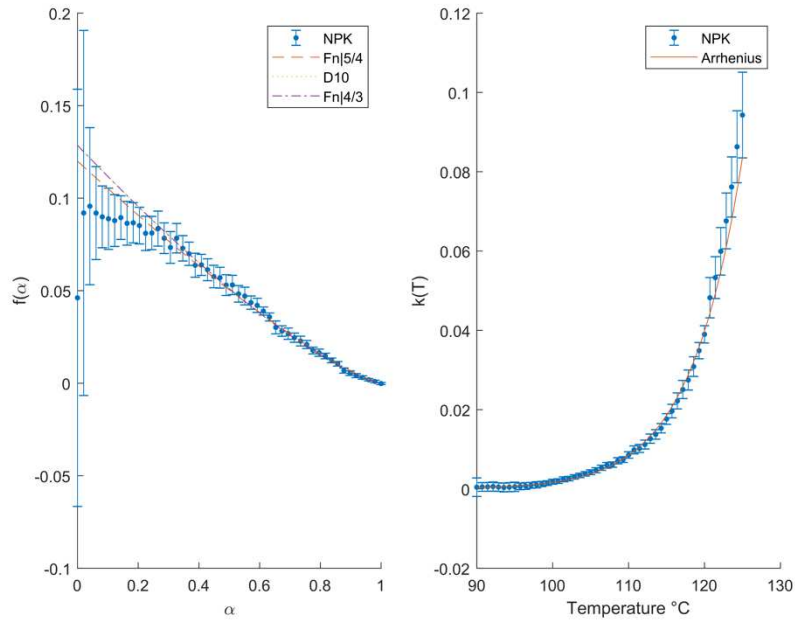


Figure 22 Reaction step 1- generated model parameter with best fitting models (left) and temperature dependency (right) evaluated via NPK method

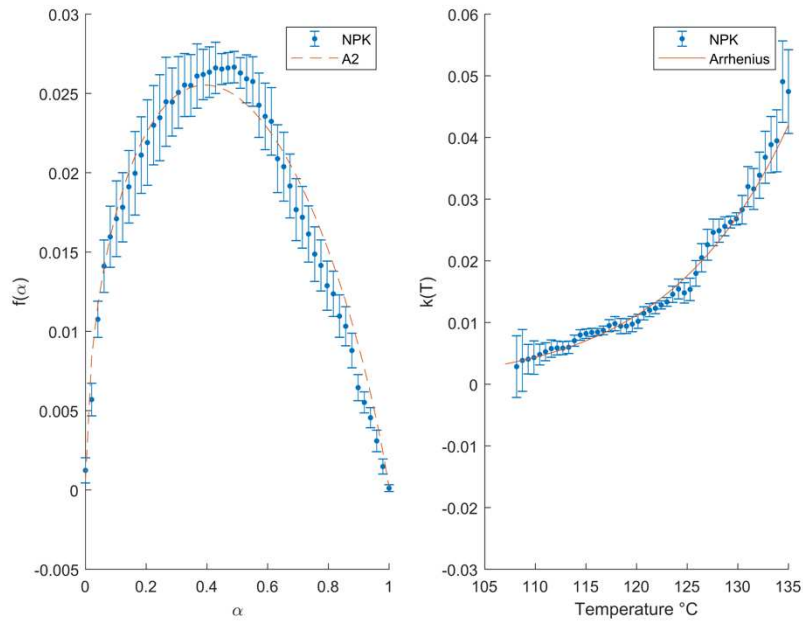


Figure 23 Reaction step 2- generated model parameter with best fitting models (left) and temperature dependency (right) evaluated via NPK method

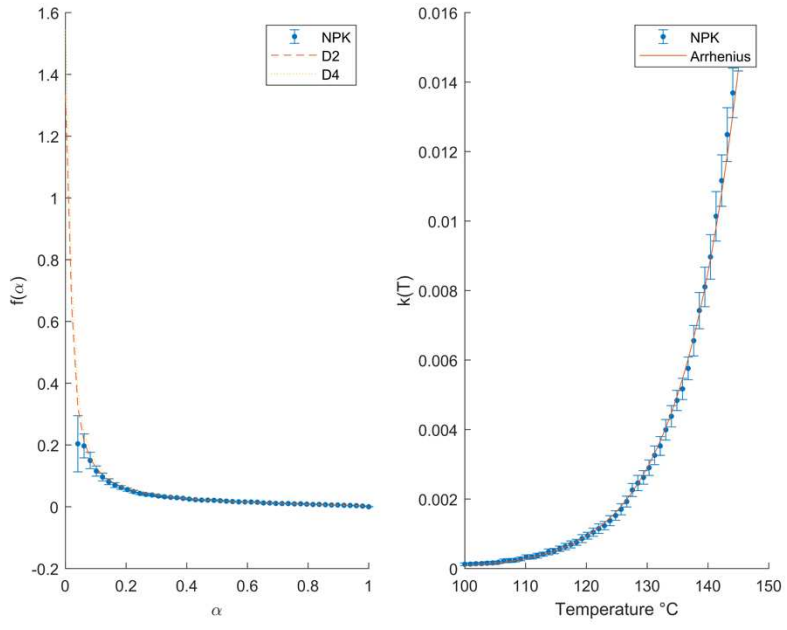


Figure 24 Reaction step 3- generated model parameter with best fitting models (left) and temperature dependency (right) evaluated via NPK method

5. Macroscopic in-depth analysis of a promising reaction system regarding its suitability as a thermochemical energy storage system

5.1. Paper II: Boric Acid: A High Potential Candidate for Thermochemical Energy Storage

This paper presents research results of the boric acid- boron oxide system regarding its suitability as thermochemical storage. The discovery of this promising reaction system was the result of a systematic research and a consecutive in-depth analysis of identified capable gas/solid reaction systems over previous years. The reaction heat was therefore analysed by means of thermogravimetric measurements and enabled the evaluation of the sample mass impact on the reaction, the reaction's energy content and the volatility of boric acid in the presence of vapour. Macroscopic investigations of the hydration of boron oxide and the volatility of boron oxide during the decomposition, analysed via a simple test rig, complemented the studies on this reaction system. Furthermore, analyses of material properties such as particle size, particle shape, crystalline structure or thermal conductivity/diffusivity were conducted, regarding their impact on the thermochemical storage material.

Results and discussion

First, thermogravimetric results revealed the impact of the sample mass and were presented in Figure 25. The results revealed the hampering effect of a bigger mass on the decomposition. The smaller the sample mass, the faster the reaction progress and the lower reaction start-temperature. While sample masses above 10 mg started to decompose just below 100 °C, with a sample mass of 2 mg an initial temperature of about 70 °C was observed. Additionally, the reaction progress showed, that the final mass could be reached much earlier and at a nearly 100 °C lower temperature, by using a small sample mass. Hence, to avoid the evident mass impact on the reaction a small mass was used for the thermal analysis. Figure 26 shows the measured experimental data via STA. Besides some technical issues, the decomposition thereby revealed an average specific reaction heat of 1208 J/g. The macroscopic hydration of boron oxide showed, the reaction's capability as TCES. Despite a high water surplus, a temperature difference of nearly 45 °C was reached (Figure 27). Figure 28 presents the thermal conductivity and diffusivity of boron oxide and boric acid. Finally, while hydrating boron oxide with vapour, a temperature- (Figure 29) as well as vapour content (Figure 30) depended volatility of the formed boric acid was determined. Apparently, boric acid is highly volatile in the presence of vapour, the released vapour of the dehydrating boric acid already causing an evaporation of the not yet decomposed boric acid (Figure 31).

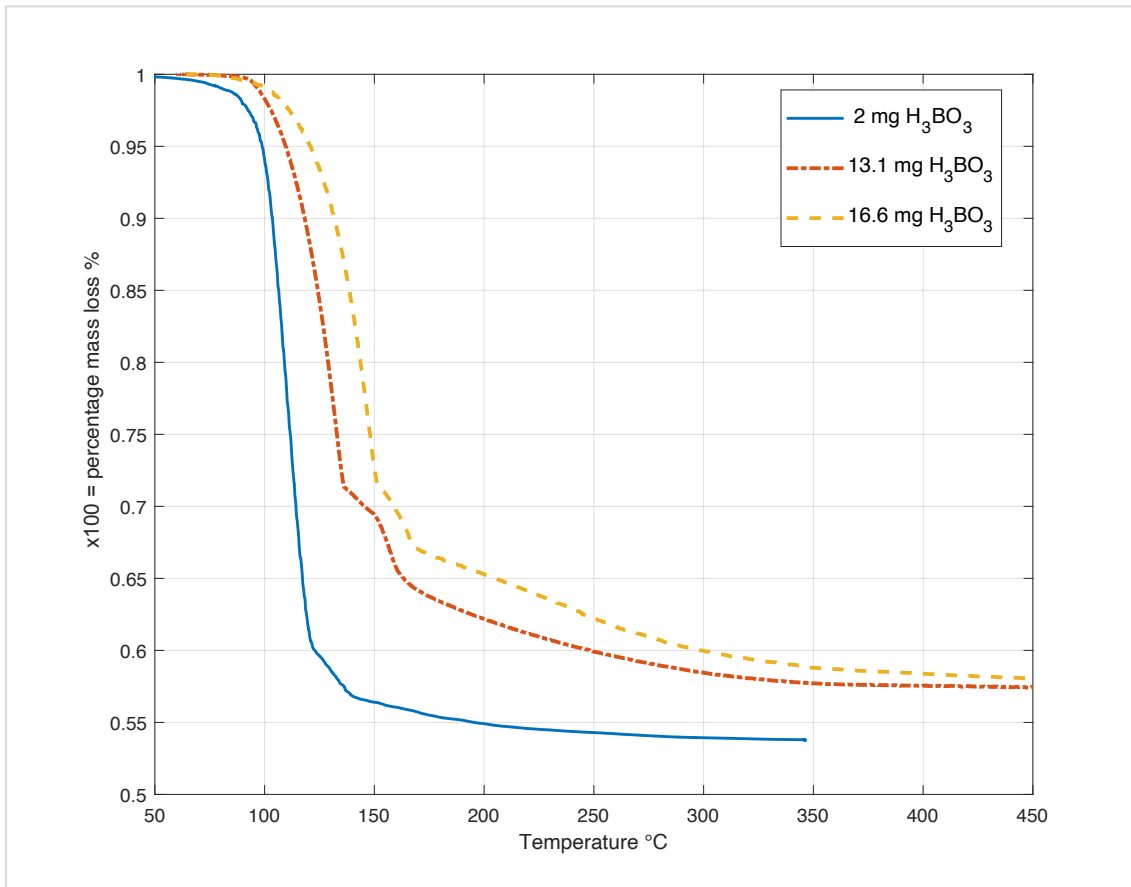


Figure 25 Decomposition process of H_3BO_3 -mass influence subject to different sample masses at heating rate of 2 °C

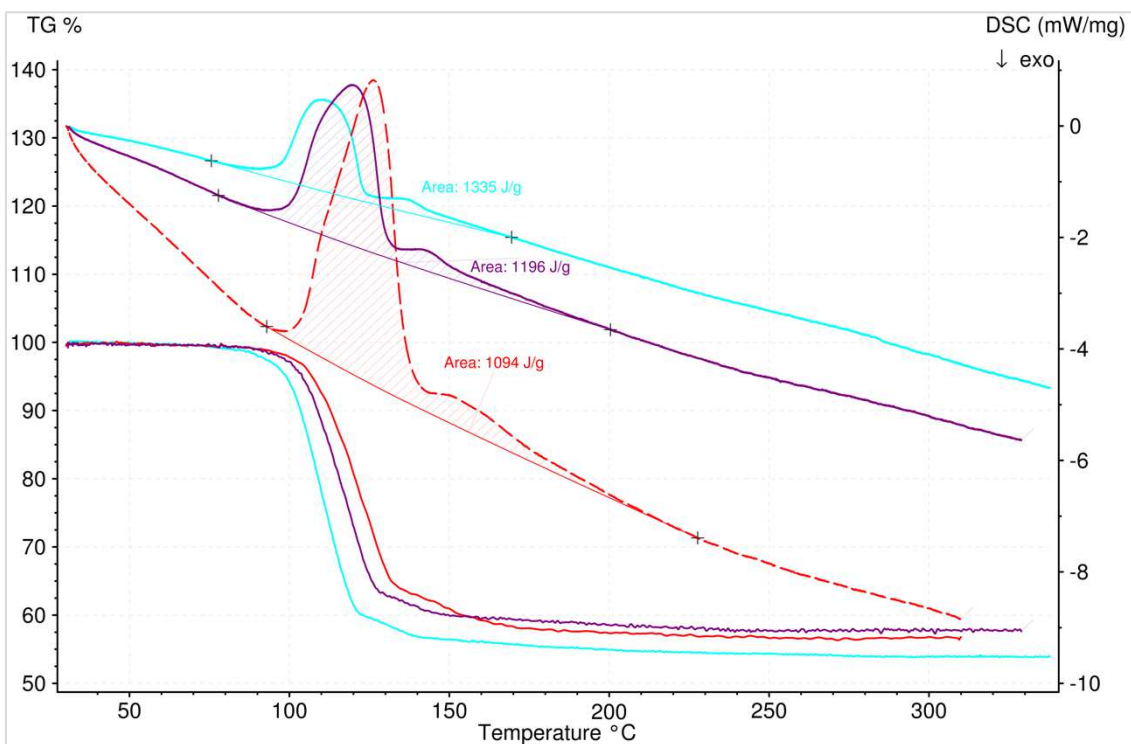


Figure 26 Thermogravimetric analyses of the decomposition of 2 mg H_3BO_3 at heating rates of 2 (turquoise), 4 (violet) and 8 (red) °C/min with the reaction's specific energy content

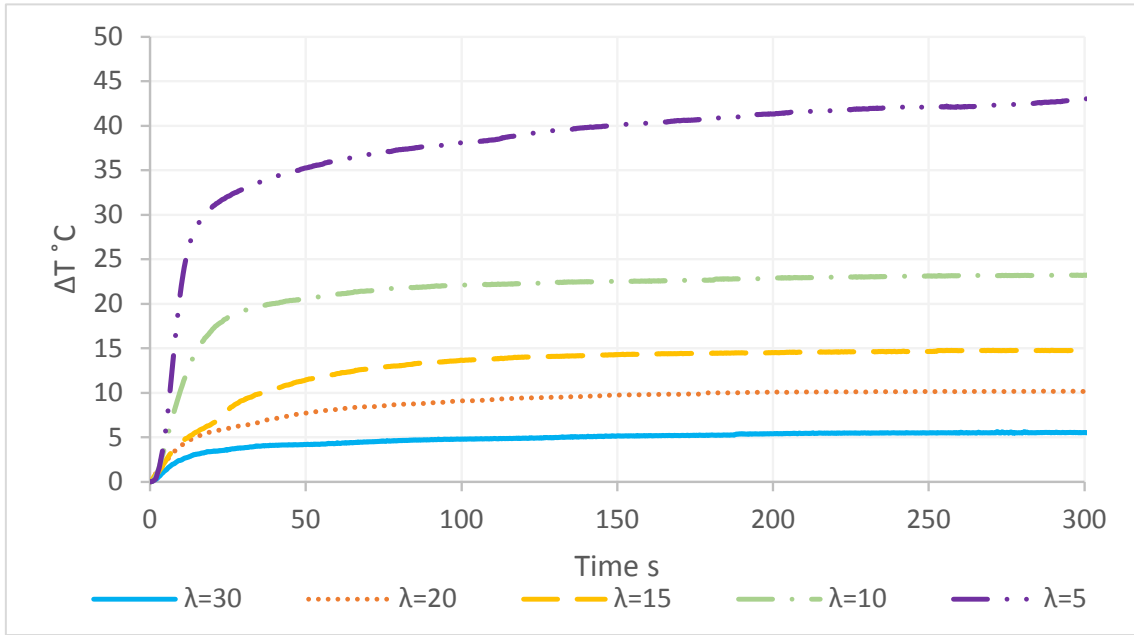


Figure 27 Temperature rise of the hydration reaction depending on different water surplus ratios (λ) with a common initial temperature of 25 °C

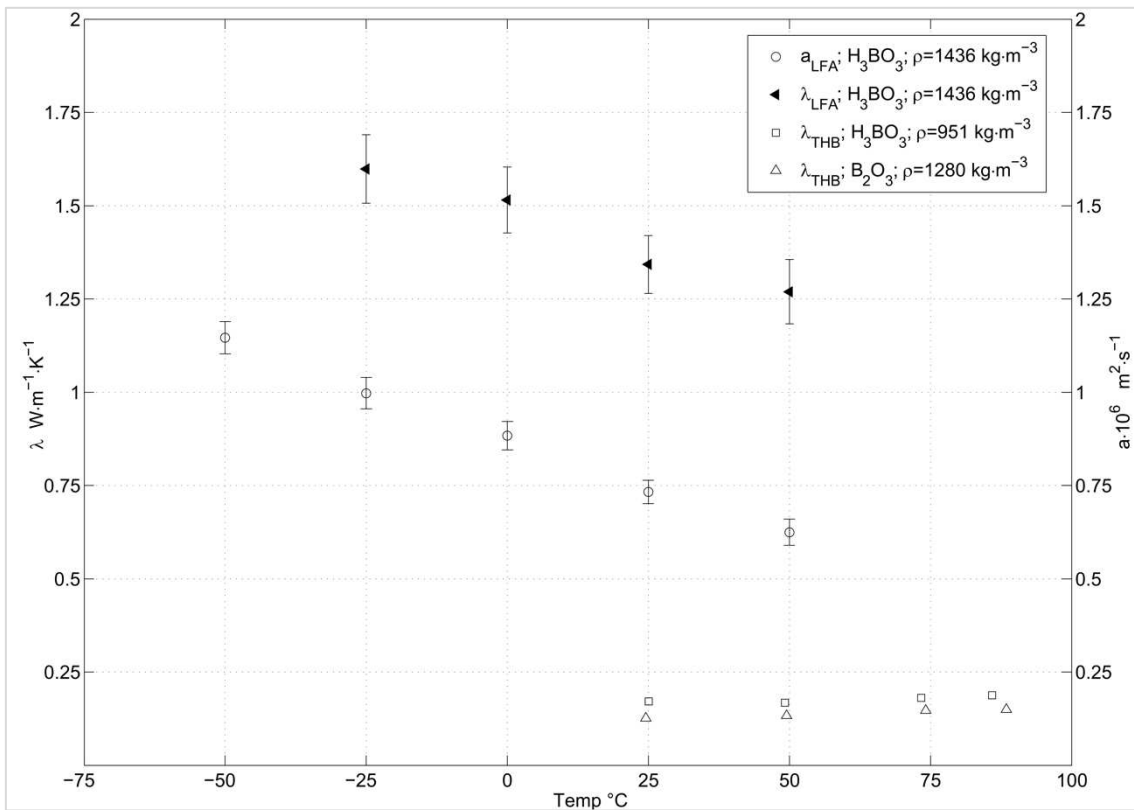


Figure 28 Thermal conductivity (λ) and thermal diffusivity ($a \times 10^6$) for B_2O_3 and H_3BO_3 (pellet and powder)

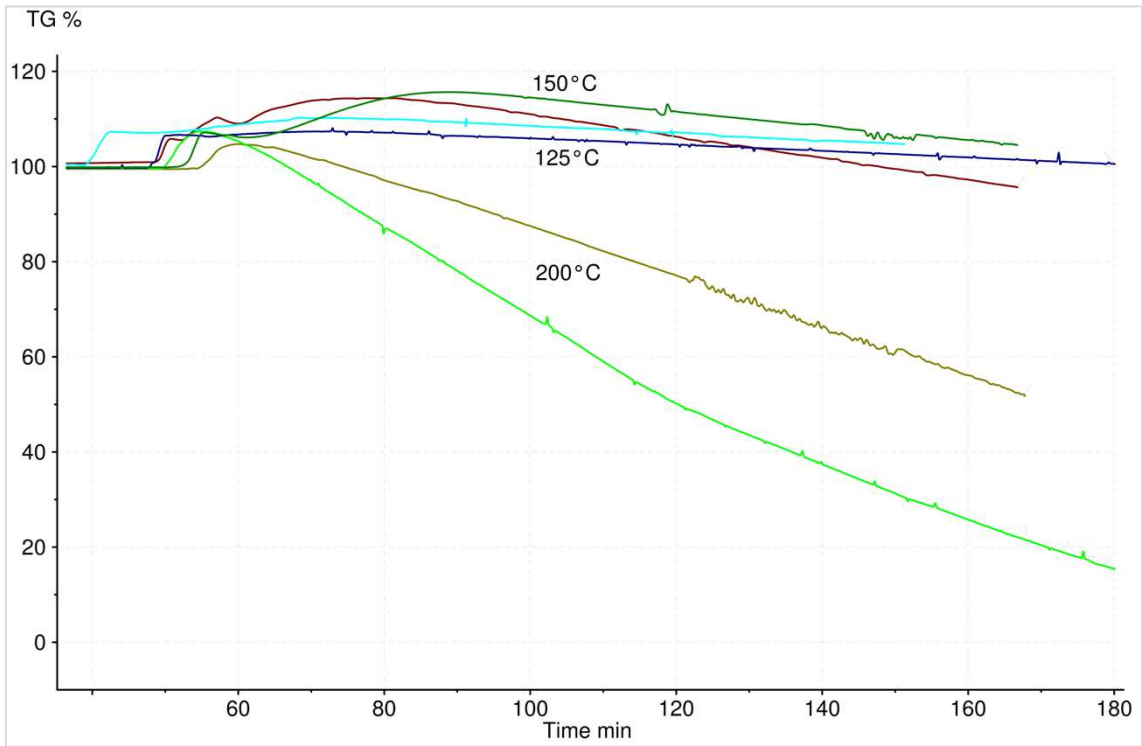


Figure 29 Hydration of B₂O₃ at constant water vapour mass flow (5 g/h H₂O within 100 mL/min N₂) - temperature influence in the volatility of the resulting H₃BO₃

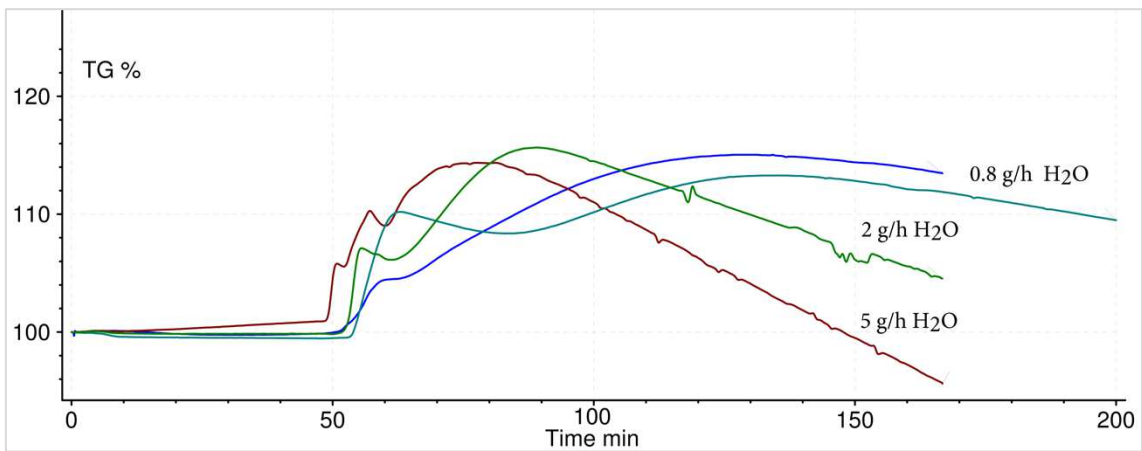


Figure 30 Hydration of B₂O₃ at constant temperature of 150 °C - volatility of the resulting H₃BO₃ depending on various water vapour mass flows

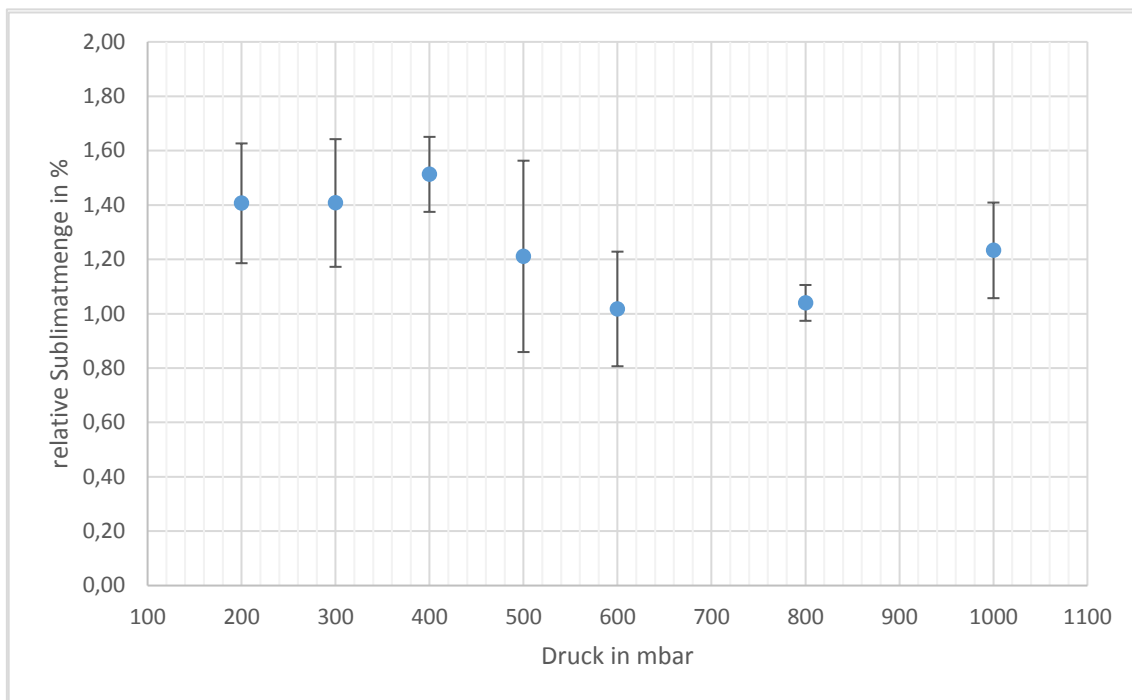


Figure 31 Volatility of 2.5 mg H_3BO_3 heated up to a temperature of 200 °C, as a function to absolute pressure

6. Conclusion and future work

6.1. Conclusion

The greenhouse effect and its ubiquitous consequences are, without doubt, one of the biggest threats for the existence of mankind. Since the industrial revolution, the world has been facing a de-facto unstoppable rise in global energy demand and the associated emissions. However, up until now, irrelevant whether for convenience or economic reasons, the resultant threat of global warming and the risks involved were mostly deliberately neglected and planned energy reforms either remained a lip service or became implemented only half-heartedly. Nowadays, we are facing the far-reaching global consequences and the public call for energy without harmful emissions, as well as a mitigation of the greenhouse effect, is growing increasingly louder every day. A general solution though, is anything but easy and cannot be implemented quickly.

Thermochemical energy storages (TCES) are considered by many scientists and politicians to be an important milestone for an overdue energy revolution, off from fossil based and therefore CO₂ emitting energy sources and towards an energy provision, based on clean energy sources without any lasting ecological footprint. So far, the respective intrinsic characteristics of the various sustainable energy sources (e.g. sun, wind, hydro- and tidal power) were not corresponding to the actual human energy demand and consequently caused a time and location gap in the energy supply. Sustainable energy therefore plays no significant role in the global energy mix yet. However, by serving as an energy buffer, TCES can act as a bridging technology, ensuring that the unsteady clean energy provision will match the real demand. Furthermore, TCES will help to harness and reuse excess heat from industrial processes and thereby will boost the efficiency of such industrial processes. An increased sustainable energy provision share and energy efficiency will hopefully lead to the aspired massive prospective mitigation of the greenhouse effect and its severe global consequences.

This thesis's main task was to elucidate different promising chemical reactions systems with a high energy density regarding their suitability for storing thermal energy. For the description of the reaction's progress as well as its different influencing factors, kinetic parameters are, amongst others, important information. Thus, this work's findings will form the next step in the development and the proper design of a thermal energy storage reactor.

Copper oxide (Paper III) is, due to its high energy density (3.6 GJ/m³) and its reaction temperature ranging up to 1000 °C, considered as a promising TCES for high temperature application. Explorations of the influences on the reaction were crucial information for the understanding and will enable an ideal process design. Nevertheless, up until now performed kinetic analyses were unable to evaluate the pressure influence and therefore neglected the mathematical evaluation of the pressure influence

term for the kinetic of this reaction. In contrast to these works, we evaluated the pressure influence term, by using the non-parametric kinetic method 2 (Birkelbach et al., 2019) and a reparametrised pressure parameter. Aside the kinetic triplet ($f(\alpha) = A2$, $A = 5 \cdot 10^9$ 1/s and $E_a = 233$ kJ/mol), the analysis revealed for the first time the significant oxygen partial pressure influence on the oxidation reaction, subject to the distance to the equilibrium curve ($h(P) = a \cdot (1 - P/P^*)^{0.658}$). This is vital information for the design and optimisation of this thermal storage process.

Boric acid is a further high potential reaction system for the storage of thermal energy. Its high energy density of more than 2 GJ/m³ combined with a reaction temperature limited to 200 °C, is a suitable energy storage providing thermal energy for household application and industry sector with a low-temperature heat demand. The multistep reaction of the boric acid decomposition (Paper I) was analysed regarding the number of reaction steps and the reaction kinetics, using a combination of two new techniques, the deconvolution for the disclosure of the respective single reaction rates and the non-parametric kinetics 2 method (NPK2) for the kinetic evaluation of the kinetic triple (E_a , A , $f(\alpha)$). This methodology, applied for the first time, showed that the decomposition consists of three (mass loss related) reaction steps and that the reaction is accompanied by the formation of amorphous phases (e.g. due to melting) at temperatures below the melting point. This work provided for the first time, the respective kinetic triplet for each single step and thereby enabled the design for an appropriate storage process based on boric acid.

Further results of the research work on the boric acid reaction (Paper II) uncovered reaction characteristics, such as the influence of the mass on the reaction (partial pressure of the gaseous product), the apparent formation of an eutectic that led to a reduced melting point during the decomposition of boric acid, as well as a pressure and temperature dependent volatility of boric acid in the presence of water/vapour. The high reaction heat of this reaction system was also confirmed for the decomposition reaction. The forming reaction was not possible to analyse by simultaneous thermal analysis, because of the boric acid's volatility. The macroscopic analysis of the hydration reaction showed its potential, even though a stoichiometric hydration was prevented by agglomeration and other macroscopic effects.

6.2. Future work

The results of this thesis presented many new findings and properties of the respective reactions for the final objective of a working storage reactor, though there is still a need for further research. A final realisation of a substantially scaled up reactor for the storage of thermal energy is strongly dependent on the further exploration and analysis of the presented reactions regarding macroscopic properties and the ideal process conditions and parameter. The success of such an energy storage system is inter alia, very much contingent upon the simplicity and high efficiency of the respective chemical process.

The more and the faster energy can be stored over a long period of time (6-12 months), the higher the possibility to cover the annual energy demand using renewable energy sources and thus the less need for fossil energy sources.

For boric acid, recent research findings suggested that the decomposition is a pressure influenced reaction, with probably various (partial) pressure dependent reaction paths. A variation of both the absolute as well as the partial vapour pressure, lead to a shift of the global reaction start and end (global pressure), or just of single reaction steps (partial pressure), depending on the prevailing pressure conditions. Vacuum conditions shifted the reaction start and end towards lower temperatures, whereas higher pressure conditions caused opposite effects. The analysis of the decomposition reaction under a variation of the vapour partial pressure furthermore revealed its impact on the reaction course. A confirmation of various (pressure dependent) reaction paths and the effects of the intermediates would be an essential information, helping to avoid the suspected eutectic formation during the decomposition and thus reaching a significant simplification of the process complexity. Therefore, further and deeper analyses of the reaction and the influencing factors are recommended before a scaled up process design can be started.

Copper oxide, on the other hand, shows a degradation due to sintering effects. This causes a decreasing specific surface and consequently the cycle stability and the reaction kinetics of this storage material will suffer as a consequence. The cause of this and possible solutions to remedy the issue (e.g. using mixed materials) are desirable information.

Nomenclature

Abbreviation	Description	Unit
Wh	Watt hour	1Wh=3.6kJ
TWh	Terrawatt hour	(10^{12} Wh)
PWh	Petawatt hour	(10^{15} Wh)
Gt	Gigaton	(= 10^9 tons)
m	Mass	kg
c_p	Specific heat capacity	$\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
T	Absolute temperature	K
T_{PC}	Phase change temperature	K
ΔH	Enthalpy change	$\text{kJ}\cdot\text{kg}^{-1}$
ΔH_{PC}	Energy of the phase change	$\text{kJ}\cdot\text{kg}^{-1}$
Wt%	Weight percentage	
Q	Heat	J
ΔG	Change of Gibbs energy	
α	Extent of reaction/conversion	
S	Entropy	$\text{J}\cdot\text{K}^{-1}$
$k(T)$	Kinetic temperature dependence term	
$f(\alpha)$	Kinetic reaction model term	
$h(P)$	Kinetic pressure dependence term	
A	Frequency factor	1/s
E_a	Activation energy	kJ·mol
$m_0/ m_t/m_\infty$	Mass at Start/time t/ end	kg
β	Heating rage	$\text{K}\cdot\text{min}^{-1}$
R	Gas constant	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
p	Partial pressure	bar
p^*	Equilibrium partial pressure	Bar
$a_0; a_1, a_2, a_3$	Fraser-Suzuki Parameter for amplitude, position, half-width and assymetry	

References

- ALVA, G., LIN, Y. & FANG, G. 2018. An overview of thermal energy storage systems. *Energy*, 144, 341-378.
- ALVA, G., LIU, L. K., HUANG, X. & FANG, G. Y. 2017. Thermal energy storage materials and systems for solar energy applications. *Renewable & Sustainable Energy Reviews*, 68, 693-706.
- ARCHER, D. & PIERREHUMBERT, R. 2013. *The Warming Papers: The Scientific Foundation for the Climate Change Forecast*, Wiley.
- ARRHENIUS, S. 1896. XXXI. On the influence of carbonic acid in the air upon the temperature of the ground. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 41, 237-276.
- BELESIOTIS, V. & DELYANNIS, E. 2000. The history of renewable energies for water desalination. *Desalination*, 128, 147-159.
- BIRKELBACH, F., DEUTSCH, M., FLEGKAS, S., WINTER, F. & WERNER, A. 2019. NPK 2.0: Introducing tensor decompositions to the kinetic analysis of gas-solid reactions. *International Journal of Chemical Kinetics*, 51, 280-290.
- BODEN, T. A. & ANDRES, R. J. 2017. Global CO₂ Emissions from Fossil-Fuel Burning, Cement Manufacture, and Gas Flaring: 1751-2014. In: CENTER, C. D. I. A. (ed.).
- CABEZA, L. F., SOLE, A. & BARRENECHE, C. 2017. Review on sorption materials and technologies for heat pumps and thermal energy storage. *Renewable Energy*, 110, 3-39.
- CÁRDENAS, B. & LEÓN, N. 2013. High temperature latent heat thermal energy storage: Phase change materials, design considerations and performance enhancement techniques. *Renewable and Sustainable Energy Reviews*, 27, 724-737.
- DEUTSCH, M., BIRKELBACH, F., KNOLL, C., HARASEK, M., WERNER, A. & WINTER, F. 2017a. An extension of the NPK method to include the pressure dependency of solid state reactions. *Thermochimica Acta*, 654, 168-178.
- DEUTSCH, M., HORVATH, F., KNOLL, C., LAGER, D., GIERL-MAYER, C., WEINBERGER, P. & WINTER, F. 2017b. High-temperature energy storage: Kinetic investigations of the CuO/Cu₂O reaction cycle. *Energy & Fuels*, 31, 2324-2334.
- DEUTSCH, M., MULLER, D., AUMEYR, C., JORDAN, C., GIERL-MAYER, C., WEINBERGER, P., WINTER, F. & WERNER, A. 2016. Systematic search algorithm for potential thermochemical energy storage systems. *Applied Energy*, 183, 113-120.
- EUROPEAN COMMISSION. n.d.-a. *2020 Energy Strategy* [Online]. Available: <https://ec.europa.eu/energy/en/topics/energy-strategy-and-energy-union/2020-energy-strategy> [Accessed 06.08. 2018].
- EUROPEAN COMMISSION. n.d.-b. *2030 climate & energy framework* [Online]. Available: https://ec.europa.eu/clima/policies/strategies/2030_en#tab-0-0 [Accessed 07.08. 2018].
- EUROPEAN ENVIRONMENT AGENCY 2019. Trends in atmospheric concentrations of CO₂, CH₄ and N₂O
- GLOBAL FOOTPRINT NETWORK. 2019. *Ecological Footprint* [Online]. Available: <https://www.footprintnetwork.org/our-work/ecological-footprint/> [Accessed 06.03.2019].
- GONZALEZ-ROUBAUD, E., PEREZ-OSORIO, D. & PRIETO, C. 2017. Review of commercial thermal energy storage in concentrated solar power plants: Steam vs. molten salts. *Renewable & Sustainable Energy Reviews*, 80, 133-148.
- HULME, M. 2009. On the origin of 'the greenhouse effect': John Tyndall's 1859 interrogation of nature. *Weather*, 64, 121-123.
- INTERNATIONAL ENERGY AGENCY 2014. Heating Without Global Warming International Energy Agency
- INTERNATIONAL ENERGY AGENCY 2017. World Energy Outlook 2017.
- INTERNATIONAL ENERGY AGENCY. 2019. *Renewables 2018 - Market analysis and forecast from 2018 to 2023* [Online]. IEA. Available: <https://www.iea.org/renewables2018/heat/> [Accessed 14.05. 2019].
- KEAY, M. 2007. Energy: The long view.

- KHAWAM, A. 2007. *Application of solid-state kinetics to desolvation reactions*. University of Iowa.
- KUDER, R. 2010. Technology orientated analysis of the emission reduction potentials in the industrial sector in the EU-27. *In: TECHNOLOGY, K. R. I. O. (ed.) IEW 2010 International Energy Workshop*. Stockholm.
- MIRO, L., BRUCKNER, S. & CABEZA, L. E. 2015. Mapping and discussing Industrial Waste Heat (IWH) potentials for different countries. *Renewable & Sustainable Energy Reviews*, 51, 847-855.
- PAURITSCH, G. 2018. 100% erneuerbarer Strom – Speicherbedarf für das Stromsystem. Austrian Energy Agency.
- PEREJON, A., SANCHEZ-JIMENEZ, P. E., CRIADO, J. M. & PEREZ-MAQUEDA, L. A. 2011. Kinetic analysis of complex solid-state reactions. A new deconvolution procedure. *J Phys Chem B*, 115, 1780-91.
- RAMANATHAN, V. & ANDREW, M. V. 1997. Greenhouse Effect, Atmospheric Solar Absorption and the Earth's Radiation Budget: From the Arrhenius-Langley Era to the 1990s. *Ambio*, 26, 38-46.
- ROINE, A. 2007. HSC Chemistry® 7ed.: Outotec.
- SERRA, R., NOMEN, R. & SEMPERE, J. 1998. The Non-Parametric Kinetics A New Method for the Kinetic Study of Thermoanalytical Data. *Journal of Thermal Analysis and Calorimetry*, 52, 933-943.
- SETOODEH JAHROMY, S., BIRKELBACH, F., JORDAN, C., HUBER, C., HARASEK, M., WERNER, A. & WINTER, F. 2019. Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu₂O to CuO in Thermochemical Energy Storage. *Energies*, 12, 508.
- SVOBODA, R. & MÁLEK, J. 2012. Applicability of Fraser–Suzuki function in kinetic analysis of complex crystallization processes. *Journal of Thermal Analysis and Calorimetry*, 111, 1045-1056.
- UNFCCC. 2018. *What is the Kyoto Protocol?* [Online]. Available: <https://unfccc.int/process-and-meetings/the-kyoto-protocol/what-is-the-kyoto-protocol/what-is-the-kyoto-protocol> [Accessed 06.08. 2018].
- UNITED NATIONS. n.a.-a. *7 affordable and clean energy* [Online]. Available: <https://www.un.org/sustainabledevelopment/energy/> [Accessed 22.05. 2019].
- UNITED NATIONS n.a.-b. Sustainable development goal. *In: EMBLEM, E. S. P. W. U. (ed.)*. <https://www.un.org/>.
- UNITED NATIONS, D. O. E. A. S. A., POPULATION DIVISION 2017. World Population Prospects: The 2017 Revision, Key Findings and Advance Tables. United Nations.
- UNITED NATIONS FRAMEWORK CONVENTION ON CLIMATE CHANGE. 2019. *What is the Paris Agreement?* [Online]. Available: <https://unfccc.int/process-and-meetings/the-paris-agreement/what-is-the-paris-agreement> [Accessed 25.05. 2019].
- VDI-WÄRMEATLAS, V. 2006. 10. Auflage. Berlin, Germany: Springer-Verlag.
- VYAZOVKIN, S., BURNHAM, A. K., CRIADO, J. M., PÉREZ-MAQUEDA, L. A., POPESCU, C. & SBIRRAZZUOLI, N. 2011. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica acta*, 520, 1-19.
- VYAZOVKIN, S., KOGA, N. & SCHICK, C. 2018. *Handbook of thermal analysis and Calorimetry: Recent Advances, techniques and applications*, Elsevier.
- WEART, S. 2019. *The Discovery of Global Warming* [Online]. American Institute of Physics, center of History of Physics: 05.05. Available: <https://history.aip.org/history/climate/co2.htm> [Accessed 2019].
- ZALBA, B., MARIN, J. M., CABEZA, L. F. & MEHLING, H. 2003. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering*, 23, 251-283.

APPENDIX

Lebenslauf

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1030 Wien

Geburtsdatum: 17. Juni 1985

Staatsbürgerschaft: Österreich

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Berufserfahrung

04/2016- heute

TU Wien- Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften

Projektassistent/ Dissertant

- Forschungsgebiet: thermochemische Energiespeichersysteme für eine nachhaltige und emissionsfreie Energieversorgung.

- Mitarbeit in folgenden Forschungsprojekten:

>SolidHeat Kinetics: Erforschung von Reaktionen zur thermochemischen Energiespeicherung

>IEA-FBC TCP: Anwendung der Wirbelschichttechnologie für eine nachhaltige Energieerzeugung.

9/2014- 03/2016

Edtmayer Systemtechnik GmbH, Wien

Projektleiter/ Projektmanager Anlagenbau

- Projekten im Bereich der Energieversorgung, Lebensmittel- und Umwelttechnik (Projektkosten bis zu 1 Mio. Euro)
- Verantwortlich für Projekte im In- und Ausland (CEE Region)
- Leitung von interdisziplinären Projektteams

7/2009

RHI-AG, Wien

Abt. Credit Risk (Praktikum)

- Unterstützung bei Auftragsfreigabe und Außenstandsbetreibung, Analysen Forderungsverkauf, Auswertung zu Debitorenforderungen, Unterstützung Akkreditivabwicklung

Seit 2003

Österreichisches Bundesheer, Österreichweit

- Derzeitige Funktion: Stabsoffizier Pionierbataillon 2
- Übungen und Einsätze in versch. Führungsfunktionen (u.a. als Kompanie-Kommandant, Stabsoffizier)
- Lehrgänge und Seminare (u.a. Führungsverhalten, Führungslehrgänge, Militärisches Projektmanagement, Rhetorik, Präsentationstechnik...)

Ausbildung

04/2016-

Dissertation

TU Wien, Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften

- Thema der Dissertation: Thermochemical Energy Storage on the basis of boric acid and copper oxide – on step towards a sustainable energy provision

12/2013

Diplomstudium Verfahrenstechnik

TU Wien, Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften

- Spezialisierung: Apparate-, Anlagen- & Prozesstechnik
- Diplomarbeit: Wärmeleitfähigkeit von Hochtemperaturmaterialien
- Studium mit ausgezeichnetem Erfolg

6/2003

Matura

Bundesrealgymnasium Wien 3, Kundmanngasse,

Weiterbildung und Seminare:

TU Wien: Projektmanagement in der Forschung, Selbst- und Zeitmanagement

Institut für Offiziersweiterbildung, Militärakademie Wr. Neustadt: Führungslehrgang,

Führungsverhalten, Führungslehrgänge, Militärisches Projektmanagement, Rhetorik,

Selbst- Ziel- und Zeitmanagement, Präsentationstechnik, ...

Wehrdienst

10/2003–10/2004

Reserveoffiziersausbildung (EF)

Kenntnisse und Qualifikationen:

- Sprachen
 - > Englisch (fließend)
 - > Italienisch (fließend)
- Führerschein
 - > Klasse B, C
- Programme
 - > MS Office (sehr gut)
 - > MS Project (gut)
 - > Autocad (gut)
 - > Catia (gut)
 - > Mathcad (gut)
 - > Matlab (gut)
 - > Fluent (gut)
 - > Java (Grundkenntnisse)
 - > SAP (Grundkenntnisse)

Persönliche Eigenschaften:

Ehrgeiz, Einsatzbereitschaft, Teamfähigkeit, Organisationsfähigkeit, Aufgeschlossenheit, analytische Denkweise, Lernbereitschaft, Verantwortungsbereitschaft

Interessen:

- > Literatur, Kochen, Kultur, Reisen
- > Sport: Segeln, Skifahren, Skitouren, Wandern, Laufen, Radfahren, Reiten, Klettern

Publikationen (Auszug)

- ALVA, G., LIN, Y. & FANG, G. 2018. An overview of thermal energy storage systems. *Energy*, 144, 341-378.
- ALVA, G., LIU, L. K., HUANG, X. & FANG, G. Y. 2017. Thermal energy storage materials and systems for solar energy applications. *Renewable & Sustainable Energy Reviews*, 68, 693-706.
- ARCHER, D. & PIERREHUMBERT, R. 2013. *The Warming Papers: The Scientific Foundation for the Climate Change Forecast*, Wiley.
- ARRHENIUS, S. 1896. XXXI. On the influence of carbonic acid in the air upon the temperature of the ground. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 41, 237-276.
- BELESIOTIS, V. & DELYANNIS, E. 2000. The history of renewable energies for water desalination. *Desalination*, 128, 147-159.
- BIRKELBACH, F., DEUTSCH, M., FLECKAS, S., WINTER, F. & WERNER, A. 2019. NPK 2.0: Introducing tensor decompositions to the kinetic analysis of gas-solid reactions. *International Journal of Chemical Kinetics*, 51, 280-290.
- BODEN, T. A. & ANDRES, R. J. 2017. Global CO₂ Emissions from Fossil-Fuel Burning, Cement Manufacture, and Gas Flaring: 1751-2014. In: CENTER, C. D. I. A. (ed.).
- CABEZA, L. F., SOLE, A. & BARRENECHE, C. 2017. Review on sorption materials and technologies for heat pumps and thermal energy storage. *Renewable Energy*, 110, 3-39.

- CÁRDENAS, B. & LEÓN, N. 2013. High temperature latent heat thermal energy storage: Phase change materials, design considerations and performance enhancement techniques. *Renewable and Sustainable Energy Reviews*, 27, 724-737.
- DEUTSCH, M., BIRKELBACH, F., KNOLL, C., HARASEK, M., WERNER, A. & WINTER, F. 2017a. An extension of the NPK method to include the pressure dependency of solid state reactions. *Thermochimica Acta*, 654, 168-178.
- DEUTSCH, M., HORVATH, F., KNOLL, C., LAGER, D., GIERL-MAYER, C., WEINBERGER, P. & WINTER, F. 2017b. High-temperature energy storage: Kinetic investigations of the CuO/Cu₂O reaction cycle. *Energy & Fuels*, 31, 2324-2334.
- DEUTSCH, M., MULLER, D., AUMEYR, C., JORDAN, C., GIERL-MAYER, C., WEINBERGER, P., WINTER, F. & WERNER, A. 2016. Systematic search algorithm for potential thermochemical energy storage systems. *Applied Energy*, 183, 113-120.
- EUROPEAN COMMISSION. n.d.-a. *2020 Energy Strategy* [Online]. Available: <https://ec.europa.eu/energy/en/topics/energy-strategy-and-energy-union/2020-energy-strategy> [Accessed 06.08. 2018].
- EUROPEAN COMMISSION. n.d.-b. *2030 climate & energy framework* [Online]. Available: https://ec.europa.eu/clima/policies/strategies/2030_en#tab-0-0 [Accessed 07.08. 2018].
- EUROPEAN ENVIRONMENT AGENCY 2019. Trends in atmospheric concentrations of CO₂, CH₄ and N₂O
- GLOBAL FOOTPRINT NETWORK. 2019. *Ecological Footprint* [Online]. Available: <https://www.footprintnetwork.org/our-work/ecological-footprint/> [Accessed 06.03.2019].
- GONZALEZ-ROUBAUD, E., PEREZ-OSORIO, D. & PRIETO, C. 2017. Review of commercial thermal energy storage in concentrated solar power plants: Steam vs. molten salts. *Renewable & Sustainable Energy Reviews*, 80, 133-148.
- HULME, M. 2009. On the origin of 'the greenhouse effect': John Tyndall's 1859 interrogation of nature. *Weather*, 64, 121-123.
- INTERNATIONAL ENERGY AGENCY 2014. Heating Without Global Warming International Energy Agency
- INTERNATIONAL ENERGY AGENCY 2017. World Energy Outlook 2017.
- INTERNATIONAL ENERGY AGENCY. 2019. *Renewables 2018 - Market analysis and forecast from 2018 to 2023* [Online]. IEA. Available: <https://www.iea.org/renewables2018/heat/> [Accessed 14.05. 2019].
- KEAY, M. 2007. Energy: The long view.
- KHAWAM, A. 2007. *Application of solid-state kinetics to desolvation reactions*. University of Iowa.
- KUDER, R. 2010. Technology orientated analysis of the emission reduction potentials in the industrial sector in the EU-27. In: TECHNOLOGY, K. R. I. O. (ed.) *IEW 2010 International Energy Workshop*. Stockholm.
- MIRO, L., BRUCKNER, S. & CABEZA, L. E. 2015. Mapping and discussing Industrial Waste Heat (IWH) potentials for different countries. *Renewable & Sustainable Energy Reviews*, 51, 847-855.
- PAURITSCH, G. 2018. 100% erneuerbarer Strom – Speicherbedarf für das Stromsystem. Austrian Energy Agency.
- PEREJON, A., SANCHEZ-JIMENEZ, P. E., CRIADO, J. M. & PEREZ-MAQUEDA, L. A. 2011. Kinetic analysis of complex solid-state reactions. A new deconvolution procedure. *J Phys Chem B*, 115, 1780-91.
- RAMANATHAN, V. & ANDREW, M. V. 1997. Greenhouse Effect, Atmospheric Solar Absorption and the Earth's Radiation Budget: From the Arrhenius-Langley Era to the 1990s. *Ambio*, 26, 38-46.
- ROINE, A. 2007. HSC Chemistry® 7ed.: Outotec.
- SERRA, R., NOMEN, R. & SEMPERE, J. 1998. The Non-Parametric Kinetics A New Method for the Kinetic Study of Thermoanalytical Data. *Journal of Thermal Analysis and Calorimetry*, 52, 933-943.
- SETOODEH JAHROMY, S., BIRKELBACH, F., JORDAN, C., HUBER, C., HARASEK, M., WERNER, A. & WINTER, F. 2019. Impact of Partial Pressure, Conversion, and Temperature on the Oxidation Reaction Kinetics of Cu₂O to CuO in Thermochemical Energy Storage. *Energies*, 12, 508.

- SVOBODA, R. & MÁLEK, J. 2012. Applicability of Fraser–Suzuki function in kinetic analysis of complex crystallization processes. *Journal of Thermal Analysis and Calorimetry*, 111, 1045-1056.
- UNFCCC. 2018. *What is the Kyoto Protocol?* [Online]. Available: <https://unfccc.int/process-and-meetings/the-kyoto-protocol/what-is-the-kyoto-protocol/what-is-the-kyoto-protocol> [Accessed 06.08. 2018].
- UNITED NATIONS. n.a.-a. *7 affordable and clean energy* [Online]. Available: <https://www.un.org/sustainabledevelopment/energy/> [Accessed 22.05. 2019].
- UNITED NATIONS n.a.-b. Sustainable development goal. *In: EMBLEM, E. S. P. W. U. (ed.)*. <https://www.un.org/>.
- UNITED NATIONS, D. O. E. A. S. A., POPULATION DIVISION 2017. *World Population Prospects: The 2017 Revision, Key Findings and Advance Tables*. United Nations.
- UNITED NATIONS FRAMEWORK CONVENTION ON CLIMATE CHANGE. 2019. *What is the Paris Agreement?* [Online]. Available: <https://unfccc.int/process-and-meetings/the-paris-agreement/what-is-the-paris-agreement> [Accessed 25.05. 2019].
- VDI-WÄRMEATLAS, V. 2006. 10. Auflage. Berlin, Germany: Springer-Verlag.
- VYAZOVKIN, S., BURNHAM, A. K., CRIADO, J. M., PÉREZ-MAQUEDA, L. A., POPESCU, C. & SBIRRAZZUOLI, N. 2011. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica acta*, 520, 1-19.
- VYAZOVKIN, S., KOGA, N. & SCHICK, C. 2018. *Handbook of thermal analysis and Calorimetry: Recent Advances, techniques and applications*, Elsevier.
- WEART, S. 2019. *The Discovery of Global Warming* [Online]. American Institute of Physics, center of History of Physics: 05.05. Available: <https://history.aip.org/history/climate/co2.htm> [Accessed 2019].
- ZALBA, B., MARIN, J. M., CABEZA, L. F. & MEHLING, H. 2003. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering*, 23, 251-283.