Iron as recyclable energy carrier: Feasibility study and kinetic analysis of iron oxide reduction

C. Kuhn\textsuperscript{a}, A. Düll\textsuperscript{b}, P. Rohls\textsuperscript{a}, S. Tischer\textsuperscript{b}, M. Börnhorst\textsuperscript{a}, O. Deutschmann\textsuperscript{a,b,*}

\textsuperscript{a} Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany
\textsuperscript{b} Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

\textbf{A B S T R A C T}

Carbon-free and sustainable energy storage solutions are required to mitigate climate change. One possible solution, especially for stationary applications, could be the storage of energy in metal fuels. Energy can be stored through reduction of the oxide with green hydrogen and be released by combustion. In this work a feasibility study for iron as possible metal fuel considering the complete energy cycle is conducted. On the basis of equilibrium calculations it could be shown that the power-to-power efficiency of the iron/iron oxide cycle is 27%. As technology development requires a more detailed description of both the reduction and the oxidation, a first outlook is given on the kinetic analysis of the reduction of iron oxides with hydrogen. Thermogravimetric experiments using Fe\textsubscript{3}O\textsubscript{4}, FeO\textsubscript{3} and FeO indicate a three-step process for the reduction. The maximum reduction rate can be achieved with a hydrogen content of 25%. Based on the experimental results a reaction mechanism and accompanied kinetic data were developed for description of Fe\textsubscript{3}O\textsubscript{4} reduction with H\textsubscript{2} under varying experimental conditions.

1. Introduction

To minimize the impact of the climate crisis, the Paris Climate Agreement was adopted in 2015, calling for limitation of the average global temperature increase to 1.5°C above pre-industrial levels \cite{1}. This requirement was reaffirmed at COP26 in Glasgow, emphasizing that achieving the 1.5°C goal will require net zero CO\textsubscript{2} emissions around mid-century \cite{2}. The achievement of this goal implies the transformation of the energy sector worldwide from fossil fuels to renewable energies. One of the key challenges is to replace coal-fired power plants as one third of the worlds electricity generation is based on coal being responsible for 30% of global CO\textsubscript{2} emissions \cite{3,4}. A stable supply based solely on renewable energies, e.g. solar and wind, must meet high demands. The production of energy from renewable resources will most likely be concentrated in places with high solar radiation or wind and underlies temporal and seasonal fluctuations. Thus, energy storage solutions are necessary which enable long-term storage, safe and easy global transportation as well as the possibility of large-scale application. Energy storage technologies include batteries, thermal and mechanical energy storage, or synthetic fuels. The suitability of energy carriers differs depending on application and requirements. Batteries, for example, have a very high efficiency (70% to 90% \cite{5}), but are only suitable for short-term storage due to their capacity \cite{6}. Green hydrogen, produced via electrolysis with electricity from renewable resources, is one widely discussed energy carrier to replace fossil fuels due to its high specific energy (33 kW h kg\textsuperscript{-1} \cite{7}). However, its usage as large-scale application for energy storage is limited due to its low volumetric energy density requiring liquefaction or compression for transportation resulting in a decrease of system efficiency \cite{8,9}.

Metal fuels are energy carriers that meet the requirements of safe and easy transportation, long-term storage and high energy density \cite{10–12}. First studies have been published that investigated metal fuels as energy carrier regarding cycle efficiency \cite{10,11,13–16}. Trowell et al. \cite{16} investigated the efficiency of aluminium as energy carrier. They state a cycle efficiency of 25% based on rough assumptions for oxidation (heat engine with 40% efficiency) and reduction (based on the energy required for primary Al production) \cite{16}. For silicon, Auner and Holl \cite{11} state a storage efficiency factor of nearly 30%. Assuming strong technology development, efficiencies of up to 40% are predicted \cite{10}. The metal powder is combusted releasing energy and forming solid metal oxides which can be easily collected. Recycling of the metal oxides is performed in areas, where sufficient and cheap green energy is available. These processes can be combined to a sustainable energy cycle, which meets the requirements of a carbon-free energy carrier and the circular economy. A proposed scheme is shown...
in Fig. 1. Attractive candidates for metal fuels are aluminium, silicon and iron due to their non-toxicity and high occurrence in the earth’s crust [17,18]. The gravimetric and volumetric energy densities of potential metal fuels in comparison to coal and hydrogen are given in Fig. 2.

In terms of volumetric energy density, metal fuels perform very well compared to hydrogen. Compared to coal, the volumetric energy density is comparable (Zn, Sn) or higher (Fe, Si, Al). Regarding the gravimetric energy density, aluminium (8.6 kWh/kg$^{-1}$) and silicon (9 kWh/kg$^{-1}$) are comparable to coal (6.4 kWh/kg$^{-1}$). The energy density of iron is lower (2.1 kWh/kg$^{-1}$) [19]. Another crucial factor is the oxidation [23]. It was shown that iron combusts heterogeneously without forming metal vapour and nanoparticles, which enables effective separation of the oxidation product [23–25]. In comparison to iron, aluminium is predicted to combust under the formation of a vapour phase leading to nanometric solid metal oxide products [23]. Additionally, it was proposed that with a burning velocity comparable to hydrocarbons and the similarities of metal powders and pulverized coal, retrofitted coal-fired power plants can be used for power generation through metal combustion [23,24]. Closing the cycle by CO$_2$-free reduction of the metal oxides is decisive for a sustainable energy system. Although current research focuses on alternatives for the carbon- and energy intensive reduction processes for aluminium and silicon, development does not yet exceed laboratory scale [11,18,26,27]. Here, electrolysis for metal production is of particular interest, since no additional intermediate step, e.g. production of the reductant, is required, which would increase the efficiency [10,28–30]. The production of iron via the electrochemical route is a current topic in research [31,32]. One of the major challenges is the dissolution of iron oxides. Beside the low temperature electrolysis in alkaline solution, the electrolysis in ionic liquids is discussed [33,34]. However, the reduction of iron oxides with green hydrogen is a key factor for reducing CO$_2$ emissions in the steel industry and proven to be applicable in large-scale [35–38], even though retrofitted steel plants with internal dry reforming processes seem to be more promising in the very near future [39]. Considering the advantages that iron has in terms of combustion and recycling, this work focuses on iron as potential metal fuel.

The reduction of iron oxide (Fe$_2$O$_3$) is a complex multistep reaction over different intermediates (FeO$_2$, FeO). A more detailed understanding is of high interest in various applications, e.g. steel industry, chemical looping or catalysis [40–42]. Numerous works focus on the elucidation of the reaction kinetics and the underlying reaction mechanism based on thermogravimetric analysis (TGA) or temperature programmed reduction (TPR) [43–46]. Pineau et al. [47] state that the reaction mechanism is a function of temperature. At temperatures below 420°C iron oxide reduction is proposed to be a two-step mechanism with FeO as intermediate. At temperatures above 570°C FeO is additionally formed before complete reduction to Fe [47]. For temperatures above 700°C Wang et al. [42] showed that the reduction Fe$_2$O$_3$ → FeO and FeO → FeO proceed simultaneously, thus the overall reduction can be seen as a two-step process Fe$_2$O$_3$ → FeO → Fe. Lee et al. [48] investigated the non-isothermal reduction of Fe$_2$O$_3$ nanoparticles. They demonstrated that the reduction steps take place consecutively and no FeO is formed as the reduction is completed below 570°C. This indicates that the crucial point of the reduction mechanism is the occurrence and stability of FeO. Thus, for a detailed understanding of the reduction mechanism, investigations regarding the reduction of the oxides FeO and FeO are decisive. Experiments on the reduction of the three oxide species were performed by Jozwiak et al. [41]. They conducted TPR measurements of FeO, FeO and FeO with 5% H$_2$ in Ar accompanied by in-situ XRD. In contrast to the publications listed above a three-stage mechanism with FeO and FeO as intermediate species independent from temperature was postulated. For temperatures below 570°C the mechanism is extended to include the disproportion of wüstite (FeO ↔ FeO + Fe) [41]. Although several studies investigate the reduction of iron oxides, the influence of varying hydrogen content has hardly been described. Wang et al. [42] studied the isothermal reduction of Fe$_2$O$_3$ with hydrogen contents from 10% to 40%. They state that the reaction rate increases linearly with increasing H$_2$ content. Kinetics of gas-solid reactions such as the reduction of Fe$_2$O$_3$ with hydrogen are normally described with a function describing the reaction process as a kinetic model, e.g. diffusion-controlled or boundary-controlled [47,49]. The kinetic models describing solid-state processes are not based on classical reaction equations relying on...
heterogeneous or homogeneous reactions but on transport processes, e.g. solid-state diffusion. This results in different rate limiting steps and apparent activation energies due to a high dependence on the experimental conditions e.g. particle size, reducing gas or the reduction temperature [40] and a lack in describing the reduction of FeO with H₂ for a wide range of conditions, which is needed for suitable process model.

The aim of the present study is to verify the feasibility of iron as energy carrier. A process simulation of the overall energy storage cycle was performed in AspenPlus® considering the reduction with hydrogen and power generation via combustion with air. The process simulation is based on equilibrium calculations. For a more detailed analysis in future, kinetic data and knowledge of the reduction and oxidation mechanism is crucial. Thus, the investigation of the thermochemical reduction of iron oxides with hydrogen is addressed in the experimental section of this paper. Non-isothermal thermogravimetric analysis of FeO₂, Fe₂O₃ and FeO with varying hydrogen concentrations and heating rates were conducted. Additionally, the experimental results were analysed and modelled for derivation of a reaction mechanism and accompanied kinetic data.

2. Methods

2.1. Process model setup

The following section describes the modelling strategy and gives an overview of the process parameters and assumptions. The overall energy cycle can be divided in two temporally and spatially decoupled processes. Since the retrofit of a coal-fired power plant is assumed for the oxidation process, the parameters are based on a real hard-coal-fired power plant (RDK-8, Karlsruhe, Germany [50]). The process is composed of a burner unit (OXI1) and the following steam turbine cycle for electricity generation. The process flow diagram of the iron oxidation unit are neglected.

The reduction process is composed of a reactor (RED1) followed by a regenerator (HX3) and the following steam turbine cycle for electricity generation. The process flow diagram of the iron oxidation can be taken from Fig. 3. The steam turbine cycle is not modelled in detail, as is equivalent to the one in RDK-8 [50]. It is therefore referred to as a blackbox process. The heat supply to the steam turbine cycle (HX1) is the intersection between burner unit (OXI1) and the steam turbine cycle. The main unit operations considered in the process simulation are summarized in Table 1. It should be noted that indicated temperatures correspond to the temperatures of the product streams in case of mixers and reactors and to the temperatures of the hot stream exiting the unit in case of heat exchangers.

The following main assumptions were made:

- The reactants iron and air are supplied to the system at 25 °C.
- The flue gas exits the burner unit with a temperature of 379 °C [51], i.e. the temperature difference between the cooled flue gas exiting the heat exchanging unit and the steam (MD) entering the heat exchanging unit amounts to approx. 20 °C.
- The temperature difference at the hot end of the air pre-heater amounts to 50 °C [51].
- Heat losses to the environment and pressure changes within the entire iron oxidation unit are neglected.

The following design specifications were defined:

- Determination of the required iron feed stream according to the steam turbine cycle’s required energy input. As a model steam turbine cycle, RDK-8 (Karlsruhe, Germany) is chosen with a gross and net electricity output of 912 and 834 MW, respectively [52, 53].
- Adaption of the air feed stream with respect to the iron feed stream in a way that the adiabatic temperature in burning unit does not significantly exceed the melting temperature of iron (Fe, 1530 °C [54]) and its main oxidation product (FeO₂, 1560 °C [54]).

The change of state of all relevant streams at the intersection of the considered control volume (burner unit) and the steam turbine cycle is given in Table 2. All mass flow rates, temperatures and pressures, except for the pressure of stream HD1 were taken from data provided for the steam turbine cycle of RDK-8 [50]. The latter was estimated on the basis of the pressure of stream HD2 under the assumption of a pressure loss of 5% in the heat exchangers of the steam turbine cycle [55].

The reduction process is composed of a reactor (RED1) followed by a regenerator (HX3), which preheats the hydrogen flux and reduces the temperature of the effluent. An electrostatic precipitator (SEP1) is used for the separation of solid iron particles. The process flow diagram can be taken from Fig. 4. The main unit operations are summarized in Table 3. It should be noted that the processes followed by the regenerator were not considered in the efficiency analysis.

The following main assumptions were made:

- The oxidized energy carrier consists of pure Fe₂O₃.
- The solid iron particles are fully separated from the gaseous effluent in the electrostatic precipitator [56].
- The temperature difference between the cooled gaseous effluent exiting heat exchanger HX3 and the hydrogen feed stream entering heat exchanger HX3 is set to 25 °C.
- Pressure changes within all units as well as heat losses to the environment are neglected.

### Table 1

<table>
<thead>
<tr>
<th>Block Description</th>
<th>Unit operation</th>
<th>T [°C]</th>
<th>p [bar]</th>
<th>x [–]</th>
<th>(\dot{m}_{\text{steam}}) [kg s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mmix</td>
<td>296</td>
<td>1</td>
<td>Mixer</td>
<td>Reactant mixing</td>
<td></td>
</tr>
<tr>
<td>RGibbs</td>
<td>1531</td>
<td>1</td>
<td>Equilibrium reactor, considered reactants: (\text{Fe, O}_2, \text{N}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MheatX</td>
<td>379</td>
<td>1</td>
<td>Heat supply to steam turbine cycle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat</td>
<td>128</td>
<td>1</td>
<td>Sep</td>
<td>Separation of solid reaction products from gaseous effluent</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Stream</th>
<th>T [°C]</th>
<th>p [bar]</th>
<th>x [–]</th>
<th>(\dot{m}_{\text{steam}}) [kg s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD1</td>
<td>305</td>
<td>321</td>
<td>0</td>
<td>652</td>
</tr>
<tr>
<td>MD1</td>
<td>360</td>
<td>62</td>
<td>1</td>
<td>542</td>
</tr>
<tr>
<td>HD2</td>
<td>600</td>
<td>275</td>
<td>1</td>
<td>652</td>
</tr>
<tr>
<td>MD2</td>
<td>620</td>
<td>58</td>
<td>1</td>
<td>542</td>
</tr>
</tbody>
</table>
The crucible was mounted on a thermocouple which is orientated was placed in an Al sample was determined by experiments carried out in this work. The specific surface area of each influence of the particle size was negligible within the scope of the μ the powders range from very small particles with a diameter of a FeO particles before milling. It can be seen that the particle sizes of are shown in Fig. 5. It should be noted that the SEM image shows behaviour is assumed to be negligible due to the mild milling conditions milled (300 r.p.m., 3 min).

2.2. Thermogravimetric analysis

For kinetic investigation of the reduction of hematite (Fe₂O₃), Sigma-Aldrich, −20 to −10 mesh) powder experimental data are derived from thermogravimetric analysis (TGA). FeO powder was ball-milled (300 r.p.m., 3 min) to obtain smaller particle sizes comparable to Fe₂O₃ and Fe₃O₄ particles. The influence of milling on the reduction behaviour is assumed to be negligible due to the mild milling conditions used. Scanning electron microscopy (SEM) images of the three sample are shown in Fig. 5. It should be noted that the SEM image shows FeO particles before milling. It can be seen that the particle sizes of the powders range from very small particles with a diameter of a few microns to larger particles with a diameter around 150 μm. The powders were sieved in advance in size fractions ranging from dₚ < 20 μm to dₚ > 67 μm to determine the influence of particle size. The influence of the particle size was negligible within the scope of the experiments carried out in this work. The specific surface area of each sample was determined by N₂ physisorption at −196 °C according to the Brunauer–Emmett–Teller (BET) method (s. Table 4). The sample mass was placed in an Al₂O₃ plate like crucible with a diameter of 17 mm. The crucible was mounted on a thermocouple which is orientated vertically inside the furnace of a Netzsch STA409. 25 ± 3 mg sample mass was used for the experiments. For all conditions, a blank measurement was performed for correction. The reduttive atmosphere consisted of hydrogen balanced with nitrogen to obtain a flow of 100 mL min⁻¹. The hydrogen content was varied from 5% to 30%. The powder samples were heated from room temperature to 900 °C with various heating rates of 2, 5, 10 and 15 K min⁻¹.

2.3. Numerical model

For kinetic analysis the thermogravimetric experiments are simulated using a zero-dimensional batch-type reactor model (DETCHEM) which is implemented in the DETCHEM program package [57] and has been used for kinetic analysis of thermogravimetric experiments in previous studies [58,59]. The model reactor consists of set of species S, which can be grouped into different phases P. For the reduction of iron oxide with hydrogen each oxide (Fe₂O₃, Fe₃O₄ and FeO) and iron is defined as single phase since mixing of solid species is not expected. Additionally, a gas phase with a volume of Vgas = 20 mL is defined. The inlet volume flux is defined based on the experimental conditions (Vin = 100 mL min⁻¹). The gas phase volume Vgas and pressure p in the reactor are kept constant. Thus, an outlet volume flux is calculated taking into account thermal gas expansion and formation of gaseous species due to chemical reaction. Phase volumes Vj are calculated according to Eq. (1). Molar volumes Vmi,j are calculated by the ideal gas law for gaseous species or expressed by constant density and molar mass for solid species. Concentrations ci of species are calculated with respect to their phase.

\[V_j = \sum_{i\in S} V_{m,i,j}\]
\[c_i = \frac{V_j}{T_j}\]

Thermodynamic properties of each species are defined by NASA-Polynomials. For Fe₂O₃, Fe₃O₄ and Fe NASA-Polynomials by Goos et al. [60] were adjusted to obtain the required format with two temperature intervals (s. supplementary material). Chemical reaction rates are based on the Arrhenius expression:

\[r_k = A_k \cdot \exp \left( -\frac{E_k}{RT} \right) \prod_j c_{i,j}^{v_{i,j}}\]

For heterogeneous reactions, which occur at the interface area A of the gas phase and a solid phase, the contact area is defined based on experimentally determined BET area of the samples (Table 4). The production rate is calculated according to Eq. (4).

\[\dot{\eta}_{k} = A_{v_{i,j}} r_{k}\]

Species and enthalpy conservation are calculated based on the following equations, where \(k_n\) is the heat transfer coefficient and \(T_{\text{ext}}\) the external temperature according the experimental conditions.

\[\frac{dQ_{n}}{dt} = \sum_{i} \dot{\eta}_{i,k} + \dot{Q}_{\text{in}} - \dot{Q}_{\text{out}}\]
\[\frac{dH}{dt} = A_k (T_{\text{ext}} - T) + \dot{Q}_{\text{in}} - \dot{Q}_{\text{out}}\]

3. Process analysis

The process is schematically depicted in Fig. 1 and can be divided in the two spatially and temporally separated subprocesses, energy storage (reduction) and energy release (oxidation). A more detailed description of the processes is given in Section 2.1. In the following, the results of the process analysis and the resulting cycle efficiency are discussed.
3.1. Oxidation

One of the main advantages of iron as recyclable metal fuel is the possibility of retrofitting coal-fired power plants which would greatly lower the hurdles for the introduction of the new technology [23,24]. The main parts that could remain would be the fuel-burning section and the steam turbine cycle [61]. Thus, the oxidation process is modelled based on data of a modern coal-fired power plant (RDK-8, Karlsruhe, Germany [50,52]). In contrast to coal-fired power plants, the combustion of iron particles leads to solid oxidation products (Fe$_2$O$_3$). This requires modifications of the process in terms of particle collection devices (s. Fig. 3). Although not considered in this work, it is interesting that the required exhaust gas aftertreatment systems would be less complex for iron-fired power plants, since only NOx formation might be a severe problem [61]. Melting and agglomeration of the iron and iron oxide particles must be considered as it might lead to blockages and deposits in the reactor or on the reactor walls. Depending on the reactor design of the reduction and oxidation processes, another objective might be to oxidize and reduce iron and iron oxide particles without intermediate adjustment of the particle sizes, which would lower the cycle efficiency. To prevent melting and agglomeration of the particles the oxidation temperature should not exceed the melting temperature of iron ($T_m$ = 1530°C [54]) and its main oxidation product (Fe$_2$O$_3$, $T_m$ = 1560°C [54]).

Thus, the dependence of the adiabatic combustion temperature on the air-to-fuel ratio ($\lambda_{\text{ox}}$) was determined (Fig. 6). At stoichiometric conditions ($\lambda_{\text{ox}} = 1$) iron reaches an adiabatic combustion temperature of 2004°C. As can be depicted from Fig. 6, the adiabatic combustion temperature decreases with further increasing $\lambda_{\text{ox}}$. For $\lambda_{\text{ox}} > 1.75$ is the combustion temperature below the melting temperature of iron and iron oxide (Fe$_2$O$_3$). Taking into account that the reactant stream is preheated, the air-to-fuel-ratio may be increased to $\lambda_{\text{ox}} = 2$ to realize an adiabatic combustion temperature below the melting points of Fe and Fe$_2$O$_3$. Another advantage of the combustion with an excess of oxygen might be the avoidance of nanoparticle formation as postulated by Töth et al. [25].

Based on the specifications, i.e. $\lambda_{\text{ox}} = 2$ and a net electricity output of 843 MW ($P_{\text{el}}$), which is specified by the model steam turbine [50,52], the oxidation efficiency is calculated:

$$\eta_{\text{ox}} = \frac{P_{\text{el}}}{m_{\text{Fe}} \cdot HV_{\text{Fe}}} \quad (7)$$

The iron feed stream of $m_{\text{Fe}} = 263 \text{ kg s}^{-1}$ is calculated to supply the necessary heat to the steam turbine cycle of RDK-8. $HV_{\text{Fe}}$ is the heating value of iron (7385 kJ kg$^{-1}$ [19]). The efficiency of the oxidation process is 43%.

3.2. Reduction

In the first step, the optimum operating parameters for iron oxide reduction with hydrogen were determined. Various equilibrium calculations were carried out at different temperatures and hydrogen ratios ($\lambda_{\text{red}}$). Fig. 7(a) shows the dependence of the iron yield on the temperature for varying hydrogen ratios. At stoichiometric conditions ($\lambda_{\text{red}} = 1$) the maximum iron yield achievable at 1000°C is 40%. An increase of the hydrogen content to $\lambda_{\text{red}} = 2$ results in a significant increase of the iron yield. Here, complete reduction is reached at 900°C. A hydrogen ratio of $\lambda_{\text{red}} = 3$ results in a complete reduction at 800°C. As can be depicted from Fig. 7(a) and (b) further increasing the hydrogen content shows only smaller effects on the yield or the reduction temperature.

Based on the request of nearly 100% iron yield and an appropriate hydrogen ratio, possible operating points were determined. Due to the very high temperatures required for reduction, hydrogen ratios of less than $\lambda_{\text{red}} = 2$ are not economically interesting. At the same time, an increase of $\lambda_{\text{red}}$ to values above 3 leads only to a slight decrease of the reduction temperature and causes technical disadvantages due to the high volume flux. Thus, in this work two possible operating points are compared. A hydrogen ratio of $\lambda_{\text{red}} = 2.8$ at a reduction temperature of 900°C (case 1) and a hydrogen ratio of $\lambda_{\text{red}} = 3$ at a reduction temperature of 800°C (case 2). Reduction efficiency is calculated according to Eq. (8), where $HV_{\text{Fe}}$ is the heating value of iron (7385 kJ kg$^{-1}$ [19]), $m_{\text{Fe}}$ the resulting iron stream and $\Delta E_{\text{red}}$ the energy required for reduction [13].

$$\eta_{\text{red}} = \frac{m_{\text{Fe}} \cdot HV_{\text{Fe}}}{\Delta E_{\text{red}}} \quad (8)$$

The two cases and the resulting efficiencies are compared in Table 5. The reduction efficiency of case 2 $\eta_{\text{red}} = 0.75$ is slightly larger than for case 1 with $\eta_{\text{red}} = 0.73$. Again, heat recovery plays a crucial role for the process efficiency. Assuming optimum heat recovery increases the efficiency to $\eta_{\text{red,opt}} = 0.91$ (case 2) or $\eta_{\text{red,opt}} = 0.90$ (case 1). Heat recovery is realized with a regenerator (Fig. 4). Depending on the particle size and process design, the resulting iron particles can...
and are recommended to be considered in a more detailed case study as reduction or oxidation and storage losses might have an effect as well. Retrieval cycles, additional effects such as material losses, incomplete material recovery or a decrease in the iron yield according to the back reaction and the residence time determine how strongly the iron will be required [10,23]. Thus, depending on the design of the reduction process an additional milling step might be necessary, which would lower the efficiency. When considering multiple storage and retrieval cycles, additional effects such as material losses, incomplete reduction or oxidation and storage losses might have an effect as well and are recommended to be considered in a more detailed case study in future investigations. To better contextualize the efficiency of the iron cycle, it is helpful to compare it to other carbon-free energy carrier, for example ammonia or hydrogen. For liquid hydrogen the following steps are assumed to determine the power-to-power efficiency [63]: Hydrogen production (70 % [62]), hydrogen liquefaction (55 % to 73 % [64]) and power generation via fuel cell (60 % [65,66]) or combined combustion (55 % to 60 % [67,68]). This results in power-to-power efficiencies of 21 % to 31 %. For CO2-free ammonia production hydrogen production via electrolysis and cryogenic air separation for nitrogen supply is assumed. Here, power consumption ranging from 7 kW h kg⁻¹ to 11 kW h kg⁻¹ is postulated, which results in power-to-ammonia efficiencies from 47 % to 74 % [68,69]. With power generation via fuel cell (56 % to 57 % [70]) or combined combustion (55 % to 60 % [67,68]) power-to-power efficiencies of 26 % to 44 % are calculated. It should be noted, that for hydrogen and ammonia the effects of storage and transportation (e.g. boil-off or cooling [63]) are not considered in the calculated efficiencies as well, since here a detailed case study would be required. The comparison with hydrogen and ammonia shows that iron can certainly be considered as a possible energy carrier. However, it also shows that it is not the efficiency of the process that is the decisive advantage, but rather the good handling capability and the possibility of using existing structures [61]. The comparison with conventional energy sources seems disillusioning at first glance. The RDK-8, operated with hard coal, achieves an efficiency of 46 % [71]. However, this efficiency only takes power generation into account. For a holistic view, external costs, e.g. for carbon capture and storage (CCS), would also have to be considered, which would significantly diminish efficiency. A review paper by Goto et al. [72] claims an efficiency penalty of around 10 % by adding CCS to existing coal-fired power plants. This shows that iron meets the requirements of an energy storage system for stationary applications. The presented study is an initial evaluation of iron as metal fuel and inevitably subject to many simplifications. Even though there has been a strong increase in research in recent years, for example to elucidate the combustion behaviour of iron [73–77], a number of research questions still need to be answered before the overall model can be described in detail. One example is the understanding of the impact of agglomeration and sintering on both the reduction and oxidation process, as it was found to occur during reduction of iron oxides in fluidized bed reactors [78,79]. Another important point is, that due to lack of data the description of the processes is only based on thermodynamic equilibrium calculations and not on kinetics of reduction or oxidation. For a more comprehensive process analysis and development of the technology an accurate

### Table 5

Comparison of the reduction cases.

<table>
<thead>
<tr>
<th>Case</th>
<th>Reduction temperature [°C]</th>
<th>Hydrogen ratio λ_{red}</th>
<th>Efficiency with optimum heat recovery η_{red,opt}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>900</td>
<td>2.8</td>
<td>0.90</td>
</tr>
<tr>
<td>Case 2</td>
<td>800</td>
<td>3</td>
<td>0.91</td>
</tr>
</tbody>
</table>

be separated from the gas stream before or after the heat recovery system. For larger particle sizes (d > 20 μm) a cyclone can be used [56]. Cyclones allow operation at high temperatures and particle separation before the regenerator. Smaller particle sizes require an electrostatic filter which cannot be operated at high temperatures [51,56]. Thus, the electrostatic filter needs to be downstream of the heat recovery system. Decreasing the temperature of the gas flux containing the iron particles might lead to a decrease in the iron yield according to the equilibrium calculations (s. Fig. 7(a)). Here, both the kinetics of the back reaction and the residence time determine how strongly the iron yield is depleted. Due to a lack of data regarding the kinetics of iron oxidation with water vapour this was not considered in this work. Nevertheless, this is an important question that needs to be addressed in future research.

#### 3.3. Cycle efficiency

Assuming efficiencies of η_{ox} = 0.43 for the oxidation and η_{red} = 0.91 (λ_{red} = 3, T_{red} = 800 °C) for the reduction process, the efficiency of the energy storage cycle is 39 % for the optimum case. With additional consideration of hydrogen electrolysis efficiency (70 % [62]) an overall power-to-power efficiency of 27 % is calculated. In this work the processes required for energy storage and energy release are considered. For a more detailed description of the overall cycle, the costs and energy losses due to transportation need to be taken into account as well. Here, the fact that oxidation leads to 43 % increase in weight should not be neglected. For the combustion process micron-sized iron particles will be required [10,23]. Thus, depending on the design of the reduction process an additional milling step might be necessary, which would lower the efficiency. When considering multiple storage and retrieval cycles, additional effects such as material losses, incomplete reduction or oxidation and storage losses might have an effect as well and are recommended to be considered in a more detailed case study.

---

**Fig. 7.** (a) Iron yield of the reduction depending on the hydrogen ratio and the temperature and (b) minimum reduction temperature (T_{red,min}) for complete reduction in dependence on the hydrogen ratio (λ_{red}).
model for iron oxide reduction and oxidation is required. Thus, the next section of this work focuses on the reduction of iron oxide with hydrogen.

4. Experimental results and kinetic analysis

In the experimental section results of the reduction of iron oxides with hydrogen based on thermogravimetric analysis are presented and discussed with respect to the reaction mechanism and kinetic parameters.

4.1. Thermogravimetric analysis

The reduction of iron oxide (Fe$_2$O$_3$) with hydrogen is investigated based on thermogravimetric analysis. Fig. 8 shows the results of thermogravimetric experiments with 10% H$_2$ and varying heating rates. The overall mass loss is approximately 30% for each heating rate which corresponds to the mass loss due to reduction from Fe$_2$O$_3$ to Fe (30.1%). The deviations of up to 2% from the theoretically achievable mass loss can be attributed to measurement errors due to the buoyancy effect, although a correction measurement was performed for each experiment. The reduction is completed for all heating rates below 800°C. The reduction starts at $T = 370°C$ for a heating rate of 2 K min$^{-1}$ and is slightly shifted to higher temperatures with increasing heating rate ($T = 440°C$ with 15 K min$^{-1}$). A more detailed examination of the mass loss graphs shows, that the reduction consists of two well divided stages, which can be seen more clearly in the derivative shown in Fig. 8(b). The first stage ranging from 370°C to 420°C for 2 K min$^{-1}$ corresponds to a mass loss of approximately 3%. This refers to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ (3.3%) according to Eq. (9). The second stage, consisting of a mass loss of approximately 27% would then correspond to the reduction of Fe$_3$O$_4$ to Fe according to Eq. (10) (26.7%). For a heating rate of 2 K min$^{-1}$ the second reduction step ranges from 420°C to 540°C. Non-isothermal TGA measurements with various heating rates are characterized by an almost parallel shift of the TGA curve to higher temperatures with increasing heating rate [49].

As can be depicted from Fig. 8, the shift of the experimental curve with increasing heating rate is more pronounced for higher temperatures. The reduction is completed at $T = 540°C$ for 2 K min$^{-1}$ while for 15 K min$^{-1}$ the reduction is completed at $T = 715°C$. This effect suggests that the reduction might be additionally retarded for high heating rates due to sintering effects that are intensified at higher temperatures [44, 46, 48]. Several authors showed that reduction of Fe$_2$O$_3$ with hydrogen produces a compact iron layer [44, 46, 48]. The reduction requires diffusion of hydrogen to the iron/iron oxide interface and diffusion of formed water molecules towards the gas phase. The formation of a dense iron layer reduces the diffusion rates of both hydrogen and water and leads to a decrease of the reduction rate at higher temperatures. It is postulated by Kim et al. [80], that the reduction proceeds by diffusion of O-atoms through the dense iron layer to the particle surface, where they react with hydrogen. Reduction leads to a decrease of the BET surface area from 3.37 m$^2$ g$^{-1}$ to 0.74 m$^2$ g$^{-1}$. A decrease of the specific surface area due to reduction was also investigated by Lee et al. [48] and Hessels et al. [81]. Beside the formation of a dense iron layer this might also be an effect of sintering and pore coalescence. This is confirmed by Hessels et al. [81], who found that with increasing reduction temperature the number of pores decreases and pore size increases. However, delaying the reaction results in better resolution of the reaction steps as can be depicted from the DTG graphs (Fig. 8(b)). It can be clearly seen that the reduction consists of at least two well divided steps. Taking a closer look at the derivatives of 10 K min$^{-1}$ and 15 K min$^{-1}$ a shoulder on the left side of the second peak (490°C to 590°C) could be an indication of an additional reduction step. As the temperatures are above 570°C, which is the key temperature for FeO stability, the reduction from Fe$_2$O$_3$ to Fe could possibly be further divided in the steps Fe$_2$O$_3$ → FeO and FeO → Fe according to Eqs. (11) and (12).

$$3 \text{Fe}_2\text{O}_3 + 4 \text{H}_2 \rightarrow 2 \text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{O} \quad (9)$$

$$\text{Fe}_2\text{O}_3 + 4 \text{H}_2 \rightarrow 3 \text{Fe} + 4 \text{H}_2\text{O} \quad (10)$$

$$\text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3 \text{FeO} + \text{H}_2\text{O} \quad (11)$$

$$\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \quad (12)$$

The influence of varying hydrogen content on the reduction of Fe$_2$O$_3$ was investigated with a heating rate of 2 K min$^{-1}$ to prevent sintering effects from superimposing the kinetics. Fig. 9 shows the reduction of Fe$_2$O$_3$ with hydrogen contents of 5%, 10%, 20%, 25% and 30% in the gas phase with a heating rate of 2 K min$^{-1}$. Increasing the hydrogen content leads to a shift of the reduction curve to lower temperatures. The reduction with 10% H$_2$ starts at 370°C and is completed at 540°C while the reduction with 30% H$_2$ starts at the same temperature but is completed at slightly lower temperatures (500°C). This implies that higher hydrogen contents lead to an increase of the reaction rate. Comparing the reduction with 20%, 25% and 30%
Fig. 9. (a) Experimental data of the reduction of Fe$_2$O$_3$ with hydrogen contents varying from 5% to 30% and a heating rate of 2 K min$^{-1}$ and (b) the resulting DTG graphs. For hydrogen contents above 25% a maximum reduction rate is reached.

Fig. 10. (a) Thermogravimetric experiments and (b) the resulting DTG graph of the reduction of the oxides Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO with 30% H$_2$ in N$_2$ and a heating rate of 2 K min$^{-1}$.

hydrogen indicates that increasing the hydrogen concentration from 25% to 30% does not lead to a further shift of the TGA curve. This suggests that with a hydrogen content of 25% an equilibrium state is reached. Wimmers et al. [82] and Zieliński et al. [45] demonstrated by TPR experiments that the reduction rate is affected by the amount of gaseous H$_2$O. They showed that the reduction rate is strongly retarded with increasing water content which is more pronounced for the reduction of Fe$_3$O$_4$ according to Eq. (10). The retardation of the reaction is not only explained by thermodynamic considerations, e.g. occurrence of the backward reaction, but also by kinetic limitations or blocking of reaction sites [45]. Conversely, this implies that with a hydrogen content of 25% the retardation effects of water vapour which is formed during the reaction are negligible and the maximum reduction rate is reached. In addition to the reduction of Fe$_2$O$_3$, the reduction of Fe$_3$O$_4$ and FeO with 30% H$_2$ were examined. The resulting TGA graphs and corresponding DTG curves are shown in Fig. 10.

For better comparability Fe$_3$O$_4$ and FeO TGA curves are depicted according to the theoretically expected mass losses of the reduction sequence Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO. For all three oxides reduction is completed for temperatures around 500°C. The start of the reduction differs slightly for the oxides but is in the same temperature range. The reduction of Fe$_3$O$_4$ starts at 340°C. The reduction of Fe$_2$O$_3$ starts at 370°C and the reduction of FeO at 395°C. Although the BET area of the FeO sample is smaller (0.26 m$^2$ g$^{-1}$) than of the Fe$_3$O$_4$ (2.44 m$^2$ g$^{-1}$) and Fe$_2$O$_3$ (3.37 m$^2$ g$^{-1}$) powder samples, it seems not to have a decisive influence on the reduction progress at this high hydrogen contents. This might be due to the high diffusivity of hydrogen. The development of the reduction of Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO is comparable as an almost parallel shift over the complete temperature range can be observed. For the oxides Fe$_2$O$_3$ and FeO only one reduction step can be detected. This underlines that the reduction of Fe$_3$O$_4$ is divided in two steps whereas the first step can be characterized as reduction to Fe$_3$O$_4$ (Eq. (9)). The second step cannot be further defined based on the experimental data, as the reduction curves do not show any characteristic features which would indicate an additional reduction step. However, a multistep reduction of the second step cannot be excluded as overlapping of reactions may occur. Additionally, the occurrence of FeO in the Fe$_2$O$_3$ reduction process due to comproportionation or the corresponding
disproportionation of FeO to Fe$_3$O$_4$ and Fe is not characterized by a loss of mass.

### 4.2. Reaction mechanism and simulations

For kinetic analysis the experimental results presented in Section 4.1 are simulated with the software package DETCHEM$^\text{MPTR}$, which is described in Section 2.3. Based on the experimental results and literature predictions a reaction mechanism for iron oxide reduction with hydrogen was developed. In a previous analysis it could be shown that the particle size ($d_p < 20 \mu m$ to $d_p > 67 \mu m$) has no influence on the reduction behaviour (s. Section 2.2). Therefore, it is concluded that transport limitations can be neglected. It is assumed that the reduction of Fe$_2$O$_3$ is a three step mechanism with Fe$_3$O$_4$ and FeO as intermediate products according to Eqs. (9), (11) and (12). FeO is assumed to be an intermediate product although it might not be formed for all experimental conditions. However, the aim of this work is the development of a reaction scheme adaptable for a wide range of conditions. Thus, FeO as intermediate cannot be neglected. To ensure stability of FeO solely for temperatures above 570°C the decomposition of FeO to Fe$_3$O$_4$ and Fe is given as an equilibrium reaction according to Eq. (13). It should be noted that the underlying kinetics are not based on experimental data but solely on the requirement that FeO is not stable for $T < 570°C$.

$4 \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$ \hspace{1cm} (13)

Kinetic analysis was performed iteratively, starting with FeO. The kinetic model considers the specific surface area of the oxides used (s. Section 2.3). It is therefore assumed that the influence of the specific surface on the reduction rate, and thus the kinetic parameters, is represented by the kinetic model. This allows the inclusion of all oxides in the model, despite their different morphologies. The comparison between simulation and experimental results is shown in Fig. 11(a). FeO reduction follows a two step reaction according Eqs. (12) and (13) and shows good agreement between simulation and experiment. The reaction rate of FeO disproportionation might be slower than depicted within the simulation due to lack of data. Further experimental data e.g. DSC would be necessary for an accurate description. For simulation of Fe$_3$O$_4$ the reduction both steps according to Eqs. (11) and (12) as well as Eq. (13) are taken into account. In Fig. 11(b) both the experimental and the simulation results are depicted. It can be seen that Fe$_3$O$_4$ reduction appears to be a one step reduction for these experimental conditions (2 K min$^{-1}$ and 30% H$_2$) as no FeO is formed. This is in agreement with experimental results by Zieliński et al. [45] who postulate Fe$_3$O$_4$ reduction as one step process for high H$_2$ contents.

For the complete description of Fe$_2$O$_3$ reduction Eq. (9) is taken into account in addition to Eqs. (11)–(13). As described above and shown in Fig. 9 increasing the hydrogen content accelerates the reduction process since the influence of the backwards reaction decreases. Thus, for the complete description of Fe$_2$O$_3$ reduction, both the backwards reaction for Fe$_3$O$_4$ and FeO reduction according to Eqs. (14) and (15) are taken additionally into account. The influence of the backwards reaction is negligible for FeO and Fe$_3$O$_4$ reduction according to Fig. 11 due to the high hydrogen content. The backwards reaction of Fe$_3$O$_4$ reduction (Eq. (9)) is not considered as it was shown by Lorente et al. [83], that it is nearly irreversible.

$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$ \hspace{1cm} (14)

$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2$ \hspace{1cm} (15)

Fig. 12 shows the experimental and simulation results of the reduction of Fe$_3$O$_4$ with 5% and 30% hydrogen and the predicted formation of the intermediate reaction products Fe$_3$O$_4$ and FeO. The retardation of the reduction process due to an increased H$_2$O to H$_2$ ratio is well predictable with the kinetic data. The simulations show, that for 5% hydrogen three reduction steps Fe$_3$O$_4$ → Fe$_2$O$_3$ → FeO → Fe can be distinguished whereas for higher hydrogen contents FeO reduction is very fast and thus formation of FeO is not observed. This shows that the hydrogen content does not only affect the reaction velocity but also the apparent reaction mechanism. This is in contrast to several authors who state solely the temperature as crucial point for FeO formation [41,46,47].

To analyse whether further increasing the hydrogen content accelerates the reduction velocity, simulations were performed with 5% to 100% H$_2$. It can be shown that increasing the hydrogen content from 30% to 100% causes only a small increase in the reaction rate (s. supplementary material). For further validation of the postulated reaction mechanism and kinetic data, simulations were also performed for experiments with varying heating rates according to the experiments shown in Fig. 8(b). As described above increasing the heating rate leads to a strong shift of the TGA curve to higher temperatures, especially for the second reduction step. Based on the simulations it can be shown that this is not only an effect of sintering processes but also of the deceleration of Fe$_3$O$_4$ reduction and the formation of FeO due to the backwards reactions which play a more important role at lower residence times (Fig. 13). The predicted mechanism and kinetic data...
show good agreement for all heating rates (s. supplementary material). All simulations were conducted with the kinetic data summarized in Table 6. A comparison between the thermodynamic equilibrium calculations and kinetic simulations shows good agreement, although deviations can be observed for small $\lambda_{\text{red}}$ and high reduction temperatures (s. supplementary material). The model presented in this work is a global kinetic model. This model will be further developed to a microkinetic model in the future. This includes e.g. the resolution of the reactions into elementary steps but also the consideration of solid phase diffusion, e.g. diffusion of oxygen atoms over vacancies in the lattice.

5. Conclusion

In this work, the feasibility of iron as energy carrier is investigated. An analysis of the overall energy cycle was conducted. Based on equilibrium calculations with the simulation software AspenPlus® the efficiency of the reduction process is predicted to be 91% and 43% of the oxidation process. With a hydrogen production efficiency of 70% this results in an overall cycle efficiency of 27%. For a more comprehensive process analysis and development of the technology an accurate reaction kinetic model for iron oxide reduction and oxidation is required. Thus, the reduction of iron oxide with hydrogen was investigated based on thermogravimetric experiments. It could be shown that the reduction process can be divided in two stages. The reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ and the reduction of Fe$_3$O$_4$ to Fe, where FeO might be an intermediate product. Based on the experimental results a reaction mechanism and the associated kinetic data for Fe$_2$O$_3$ reduction with hydrogen is postulated. It is assumed that the reduction of Fe$_2$O$_3$ is
a three-step process with Fe$_2$O$_4$ and FeO as intermediate products. In addition, it was demonstrated that the backwaeks reactions of Fe$_2$O$_4$ and FeO reduction have a decisive influence on the course of the reaction and the apparent reaction mechanism. For further verification of the mechanism additional investigations e.g. by differential scanning calorimetry, in situ XRD or analysis of intermediate reduction steps are of high interest and will be addressed in future. The predicted model needs to be further refined regarding the effect of sintering and the resulting change of the surface area during the course of the reduction as well as transport limitations that might occur. The influence of the backwaeks reactions is an important factor, that needs to be considered in a detailed description of the reduction process. In a more detailed case study it is recommended to determine which kind of reactor, e.g. fluidized bed, blast-furnace or rotary drum reactor is the most promising. Beside the reduction, elucidation of the oxidation kinetics is also an important task that will be addressed in future research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was performed within the cluster project Clean Circles. Financial support by the Strategy Fund of the KIT Presidium is gratefully acknowledged. Furthermore, we acknowledge Steinbeis GmbH & Co. KG für Technologietransfer (STZ 240 Reaktive Strömung) for a cost-free license of DETCHEM.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jaecs.2022.100096.

References

null