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Dynamic simulation of isothermal and non-isothermal reduction and oxidation reactions of iron oxide for a hydrogen storage process

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Abstract: This work aims first to develop a dynamic lumped model for the isothermal reactions of hydrogen/steam with a single iron oxide/iron pellet inside a tubular reactor and to validate the model results against the experimental reaction kinetic data with the help of our STA device. To describe the temporal change in mass, and consequently, the temporal heat of reaction, the shrinking core model, based on the geometrical contracting sphere, is applied. It turned out that, the simulation model can reproduce the experimental, temporal concentration and temperature-dependent conversion rates with a maximum deviation of 4.6% during the oxidation reactions and 3.1% during the reduction reactions. In addition, a measured isothermal storage process comprising one reduction and one oxidation phase with a holding phase in between on a single reacting pellet could be reproduced with a maximum absolute deviation in the conversion rate of 1.5%. Moreover, a lumped, non-isothermal simulation model for a pelletized tubular redox-reactor including 2 kg of iron oxide pellets has been established, in which the heat of reaction, heat transfer to the ambient and heat transfer between the solid and gas phases are considered. The temporal courses of the outlet gas concentration as well as the temperatures of the gas stream and the solid material at a constant input gas flow rate and a constant reacting gas inlet concentration but different input gas temperatures are estimated. Because of the endothermic nature of the reduction reaction, the inlet reacting gas temperature shall be kept high to prevent the severe temperature drop in the solid phase and, consequently, the significant reduction of the reaction rate. Contrary to that, the oxidation process requires lower input gas temperatures to avoid the excessive overheating of the reaction mass and, consequently, the sintering of the reacting pellets. Finally, five of the previous reactors have been connected in series to explore the influence of the changing inlet gas temperatures and concentrations on the dynamic performance of each storage mass.

Keywords: hydrogen storage; iron/iron oxide; redox reactions; lumped model; isothermal reactions; non-isothermal reactions; kinetics of reactions; Aspen Custom Modeler

1. Introduction

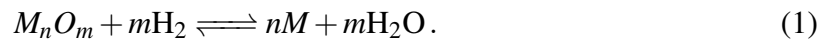
According to the IPCC, human activities are responsible for a significant global temperature rise compared to the pre-industrial age, leading to adverse effects which have become more and more serious in recent years [1]. The reason behind this development is identified in the



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global greenhouse and CO₂ gas emissions. Although these are periodically flattening out, they have increased by an average of 1% per year over the last ten years [2]. The main part of these emissions can be attributed to energy systems dominated by fossil fuels [1,2]. To mitigate such developments, a global transformation to “green” energy forms deems absolutely necessary. One potential solution could be a smart combination of wind, solar, as well as bio-energy with efficient energy storage technologies and recovery systems [3,4]. Hydrogen as an energy carrier, offers ideal conditions for a cross-sectional “green” energy supply. It can be produced through an electrolyser, driven by renewable electricity, and has the potential to provide the much-needed flexibility to power systems, acting as a buffer to non-dispatchable renewable energy generation. Therefore, it can play a dominant role in seasonal balancing of renewable generation by storing large amounts of hydrogen [2].

A promising approach for hydrogen storage is the thermochemical reduction and oxidation of metal oxides (M_nO_m) / metals (M), which can be generally described by [5,6]:



Hydrogen is not physically stored within the metal bulk, instead, the oxide in the solid is stored out for the repeated oxidation of hydrogen to steam and stored in for the reduction of steam to hydrogen. Instead of storing hydrogen directly, the metal storage offers considerable safety and long-term advantages compared to, e.g., hydrogen compression or liquefaction technologies. Several metals with high oxygen binding capacity, such as Ce, Cu, Fe, Mn, Ni, and W show great storage potential and have been tested as reaction masses [7]. Because of its high availability and low cost, iron is considered to be the most suitable oxide carrier material [7–10]. Furthermore, the basis of the iron redox process, called the “steam iron process” [11], was developed in the early 20th century and has been established on an industrial scale. Nowadays, the reduction of iron oxide is mainly used in iron production processes [12,13], where natural iron ore is reduced to metallic iron by means of a H₂/CO gas mixture.

The steam iron process can be described as a heterogeneous non catalytic gas-solid reaction [14]. The overall redox process consists of an endothermic charging (reduction) and an exothermic discharging (oxidation) reaction. In general, iron (Fe) has three oxidation stages, wuestite (FeO), magnetite (Fe₃O₄) and hematite (Fe₂O₃), which take place at different partial pressures of oxygen. According to our previous work [15], the considered atmospheric pressure and process temperatures up to 800 °C exclude the third oxidation stage. The first two stages can be combined, which results in the following simplified reaction equations. During the endothermic charging phase, Fe₃O₄ is reduced by hydrogen to Fe and steam, which is described as:



The subsequent discharging or oxidation reaction, where Fe is oxidated by steam to Fe₃O₄ and hydrogen, also following the two-stage reactions, can be formulated as:



Considering the mass ratio of H₂ to Fe in equations (2) and (3), a theoretical maximum storage of hydrogen in iron of 4.8 wt% can be estimated, which is equivalent to a gravimetric energy storage density (ESD) of 1.6 kWh/(kg Fe). A mixture of 90%-wt. iron oxide and 10%-wt. stabilizing material in spherical pellets with $d = 12$ mm, which are backed inside a tubular reactor having a bed porosity of 36% results in a volumetric ESD of 2.8 kWh/(L bulk) [15]. Such a remarkable ESD of the redox storage process and the low-cost advantage of the storage material provide an excellent basis for the development of an efficient thermochemical energy storage process. Beside the application in long-term storage applications, a bunch of industrial processes do exist, in which the redox process can be excellently integrated, like e.g. the hydrogen pyrolysis process [16] or the processing of the discharged hydrogen in a solid oxide

fuel cell [17]. For these reasons, various research groups have been dealing with this type of hydrogen storage. More about the outcomes of these research groups can be read in [15, 18].

Our research group aims at developing a seasonal redox storage technology based on stable iron oxide pellets [19] and utilizing the the described redox process as a stand-alone renewable energy storage and supply system for urban quarters and industry processes. A more detailed description of the system can be read in [15].

In a previous work [20], intensive experimental and analytical investigations have been conducted to define the most appropriate kinetic model for the redox reactions and to fit the experimental data to the well-known shrinking core model allowing for both temperature- and concentration dependencies of the reaction velocity constants to be considered. This work aims first at developing a lumped dynamic model for a single iron oxide/iron pellet inside a tube to replicate the real isothermal reduction and oxidation reactions' conditions inside the thermogravimetric analyzer (TGA) device. To this aim, the model equations for energy, total and species mass balances are programmed in the Aspen Custom Modeler to simulate the change in mass over time and thus the temporal courses of the heat consumption/release rates of both reactions. The results of the developed isothermal model will be validated against our experimental data. Moreover, a non-isothermal, lumped model for a pelletized tubular redox reactor containing 2 kg of pellets is introduced. The temporal courses of the heat of reaction, heat loss to the ambient as well as the heat transfer rate between the gas and solid phases inside the reactor have been evaluated under different sets of initial, boundary and operating conditions. Finally, five of the pelletized reactors have been connected in series and their temporal performance have been evaluated to explore the effect of the varying temperature and concentration of the inlet gas stream on the conversion rate of the respective reactive mass inside each reactor.

2. Methods

In this section, the experimental setup and the investigated hydrogen storage material are described. In addition, the developed models for the dynamic simulation of the isothermal and non-isothermal reduction and oxidation reactions are presented. Finally, the tool, which is applied for conducting the simulations is introduced along with the supplementary property equations to complete the model.

2.1. Material and experimental setup

Both reduction and oxidation reactions of a single iron oxide/iron pellet has been thoroughly investigated under the isothermal conditions of 600 °C, 700 °C and 800 °C applying a thermogravimetric analyzer (STA 449-F3, Netzsch). The reduction of the iron oxide pellet is triggered by a mixture flow of nitrogen and hydrogen into the TGA device, where the sample is placed. Different gas mixtures are adjusted by means of a mass flow controller for each gas (EL-FLOW, Bronkhorst, Kamen, Germany) and fed into the TGA device. The oxidation of the previously reduced samples takes place in a gas mixture of H₂O-H₂. The required steam is produced in a steam generator (DV2MK, aDROP Feuchtemeßtechnik GmbH, Fürth, Germany) and transferred to the TGA by means of a heated metallic hose to avoid condensation. Furthermore, a vacuum pump is used to evacuate the experimental setup after each experiment for safety reasons. The measured values of the experimental setup are stored locally on the measurement computer with a sampling rate of 200 points/min. The accuracies of the applied devices are listed in Table 1.

The effect of both hydrogen and steam concentrations in the reactant stream, with nitrogen as a carrier gas, on the dynamics of the reduction and oxidation processes have been investigated. During this test campaign, the reaction kinetics of the investigated sample ($d_0 \approx 12.7$ mm, $m_0 = 3589$ mg (Fe₃O₄ and Stabilizer)) were measured at the gas mixture

Table 1. List of all measuring device accuracies for the experimental setup.

Device	Physical Unit	Measurement Accuracy
STA 449-F3, Netzsch	Mass	$35 \text{ g} \pm 0.0001 \text{ mg}$
	Temperature	$1600 \text{ }^{\circ}\text{C} \pm 0.3 \text{ }^{\circ}\text{C}$
EL-FLOW, Bronkhorst	Gas flow (H_2 , N_2)	$250 \text{ mL/min} \pm 0.5 \%$
Steam generator DV2MK, ADROP	Mass flow (H_2O)	$25 \text{ g/h} \pm 1 \%$

molar flow rate of 0.67 mol/h . During the test campaign, the molar concentrations of the reducing and oxidizing gas mixtures were changed according to Table 2 for the different redox runs (ro_1 – ro_3).

Table 2. Influx molar concentrations of the reducing and oxidation gas mixtures during the three redox experiments ro_1 to ro_3 .

Label	Reduction H_2/N_2		Oxidation $\text{H}_2\text{O}/\text{N}_2$	
	$\frac{\text{mL}}{\text{min}} / \frac{\text{mL}}{\text{min}}$	mol %/mol %	$\frac{\text{g}}{\text{h}} / \frac{\text{mL}}{\text{min}}$	mol %/mol %
ro_1	63/187	25/75	3.6/125	33/67
ro_2	125/125	50/50	6/125	50/50
ro_3	200/50	80/20	9.5/50	80/20

The experimental data corresponding to the first test condition (ro_1) as well as the reduction measurement at the second test condition (ro_2) have been taken from [20]. Dedicated measurements have been carried out under the remaining test conditions for this work. The details of the experimental set-up and the measuring procedures can be read in [20]. In addition, a storage process comprising a reduction phase followed by a storage time of almost 2 hours as well as a subsequent oxidation phase at ro_3 and $700 \text{ }^{\circ}\text{C}$ has been measured and modeled.

2.2. The Lumped isothermal model

Validated simulation models for the encountered chemical reactions in the redox-hydrogen storage process is fundamental for its design, scale-up, optimization, and, later on, its industrial application. The presented model in this section is the isothermal lumped model, which is developed for a single redox pellet under three different isothermal reaction conditions to estimate the temporal conversion rates of both reduction and oxidation reactions under different input gas flow rates and concentrations. The results obtained from that model will be validated against our experimental data [20], which have been conducted according to the operating conditions listed in Table 2. In addition, the model offers the estimation of the temporal mass of the reactive solid phase as well its temporal molar quantities of iron and magnetite. Moreover, the heat of reaction needed to be added/removed by the STA device to keep the isothermal conditions during the reduction/oxidation reactions, respectively will be presented and discussed.

The Biot-Number of the applied redox pellets is below 0.1, so that the assumption of a lumped model is validated. In addition, the gas phase stream is assumed to be an ideal gas mixture flowing over the redox pellet inside the cylindrical tube replicating the situation inside our STA device as depicted schematically in Figure 1(a) during the reduction reaction and 1(b) for the oxidation reaction.

To express the time-dependent state of reaction, the instantaneous reduction/oxidation conversion rate $\alpha(t)$ is introduced and defined by equation (4). Strictly speaking, $\alpha(t)$ articulates the instantaneous mass change of the sample $m(t)$ relative to its initial mass m_0 , divided by the equilibrium differential mass change between m_{∞} reached after an infinite reaction time and the initial sample mass m_0 . It is worth to notice here that, the initial sample mass m_0 of the iron oxide pellet consists of the initial active mass of iron oxide, which participates in the reaction (m_R) and the mass of the stabilizing material (m_{st}), which is needed

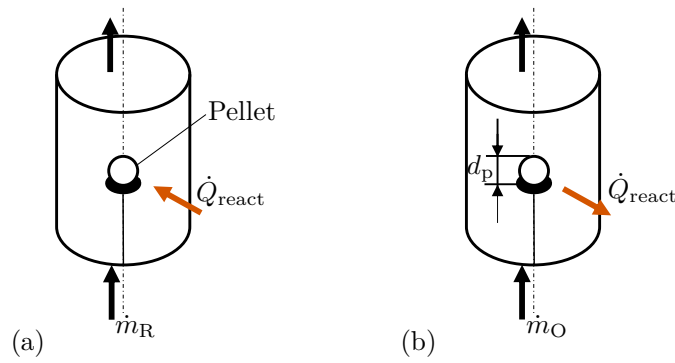


Figure 1. Sketch for a single pellet inside the TGA-reactor for deriving the lumped isothermal model (a) during the reduction reaction and (b) during the oxidation reaction.

to produce stable redox pellets, like e.g. fire cement, and is not participating in the reactions.

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

The two boundary values of equation (4) take place, first, at the beginning of the reaction, when only educt material is present and thus $\alpha(0) = 0$, and second, at the end of the reaction, where $\alpha(\infty)$ approaches one. To distinguish between reduction and oxidation reactions, the so-called oxidation fraction $u(t)$ is introduced, which describes the fraction of oxidized material in the pellet. In case of iron oxide reduction, the pellet starts as a completely oxidized solid material. As ($\alpha(0) = 0$) according to equation (4) the reduction reaction starts with an oxidation fraction of $u(0) = 1$ based on its definition by equation (5).

$$u(t) = 1 - \alpha(t) \quad (5)$$

On the other hand, during the oxidation reaction of iron, only non-oxidated material is present at $t = 0$ and so equation (6) with $u(0) = 0$ is valid.

$$u(t) = \alpha(t) \quad (6)$$

Building on the conclusions of previous studies, the shrinking core model with the geometrical contracting sphere function, will be applied to describe the reaction kinetics of the iron redox reactions [20, 21]. Assuming a spherical pellet geometry, the temporal conversion rate $\alpha(t)$ can be expressed as a function of the temporal thickness of the reaction layer of the pellet [22]. This layer represents the reactive front, where both chemical and structural changes are taking place. Accordingly, defining the initial radius $r_{p,0}$ and the radius of reaction layer within the pellet $r_k(t)$ is decisive. According to the shrinking core model (SCM), it is assumed that, both redox reactions start at the surface of the pellet, which implies that $r_k(t = 0) = r_{p,0}$. During the reaction, the reactive layer moves towards the center of the pellet, while the reaction is maintained by diffusive gas mass transport until the respective reaction is completed with $r_k(t) = 0$ [23]. The temporal conversion rate is formulated according to the SCM as a function of the described radii of the pellet by equation (7).

$$\alpha(t) = 1 - \left(\frac{r_k(t)}{r_{p,0}} \right)^3 \quad (7)$$

As already mentioned, both reduction and oxidation reactions can be described by a phase boundary-controlled reaction [20]. The following equation may be written to express the time derivative of the conversion rate as a function of the velocity rate constant and the kinetic mechanism function [21]:

$$\frac{d\alpha}{dt} = k_A \cdot f(\alpha) \quad (8)$$

The expression $f(\alpha)$ stands for the kinetic mechanism function, which is given by equation (9) for a geometric contracting sphere, which belongs to the group of phase boundary controlled reaction models [21].

$$f(\alpha) = 3(1 - \alpha)^{\frac{2}{3}} \quad (9)$$

In equation (8), k_A represents the reaction velocity rate in 1/s of the respective reaction process, which is formulated by the following Arrhenius equation

$$k_A(C, T) = A \cdot C^n \cdot e^{-\frac{E_a}{RT}} \quad (10)$$

with E_a representing the activation energy in kJ/mol, A the pre-exponential factor of the Arrhenius function in 1/s, T the absolute temperature in K and R the gas constant in kJ/(mol · K). To account for the concentration dependency of the rate constant, the molar gas fraction C is introduced and raised to the empirical exponent n [24–26]. The exponential term with the activation energy describes the temperature dependency of the respective reaction. The three parameter E_a , A and n have been already obtained by fitting the experimental data (ro₁-ro₃) as described in [20]. Accordingly, equation (11) is reported for the reduction reaction with $C = x_{H_2, in}$ as the mole fraction of hydrogen in the input gas stream and equation (12) for the oxidation reaction with $C = x_{H_2O, in}$ as the mole fraction of steam.

$$k_{A,R}(x_{H_2, in}, T) = 0.1813 \text{ s}^{-1} \cdot x_{H_2, in}^{0.75} \cdot e^{-\frac{56.9 \text{ kJ/mol}}{RT}} \quad (11)$$

$$k_{A,O}(x_{H_2O, in}, T) = 0.0023 \text{ s}^{-1} \cdot x_{H_2O, in}^{0.75} \cdot e^{-\frac{16.0 \text{ kJ/mol}}{RT}} \quad (12)$$

According to equations (11) and (12), both reaction rates increase with increasing the temperature and/or the molar concentration of the respective reactive gas. In terms of the reduction reaction, the obtained temperature dependency is consistent with the endothermic reaction mechanism. The enhanced kinetics of the oxidation reaction at higher temperatures is explained by the enhanced diffusion coefficient, which has a bigger impact on the reaction rate than the inhibited exothermic reaction because of such elevated temperatures.

The described redox reactions by equations (2) and (3) represent equilibrium reactions, where both, reduction and oxidation, are taking place at the same time. Depending on the valid temperature and partial gas pressure of the active reacting gas component, one of both reactions becomes the dominant reaction. This dependency can be described by the equilibrium constant K_{eq} , which is valid for the considered isobaric redox reactions [27]. The temperature dependency of K_{eq} follows a logarithmic correlation, as described by equation (13), according to the Van't Hoff's correlation for isobaric reactions [23].

$$\ln K_{eq}(T) = a \frac{1}{T} + b \quad (13)$$

The correlation coefficients a , b have been derived from the properties library of Aspen Plus [28] and presented in Table 3.

Table 3. Correlation coefficients for the equilibrium constant K_{eq} based on [28].

T	a	b
$T < 600 \text{ K}$	-12.342	9.634
$600 \text{ K} \leq T < 700 \text{ K}$	-11.048	8.151
$700 \text{ K} \leq T < 800 \text{ K}$	-10.180	7.260
$T \geq 800 \text{ K}$	-9.495	6.621

Complementary to equation (13), the equilibrium constant can be applied in the law of mass action, where the mole fractions of both reactants and reaction products are multiplied, with each raised to an exponent equal to its stoichiometric coefficient in the equilibrium gross

reaction equation [27]. In case of a solid-gas reaction the mole fraction corresponds to the gas components' partial pressure, while the partial pressure of the solid components being neglected [29]. Accordingly, the equilibrium constant of the redox reaction is only influenced by the mole fractions $x_{\text{H}_2\text{O}}$ and x_{H_2} .

In case of $x_{\text{H}_2,\text{in}}$ is higher than $\sqrt[4]{K_{\text{eq}}(T)} \cdot x_{\text{H}_2\text{O},\text{in}}$, the reduction reaction is triggered, otherwise the oxidation reaction takes place. The equalization of both terms would then imply the reaction equilibrium.

The already described temporal change of the pellet mass and its molar composition along with the variation in the gas mixture concentration upon flowing over the reacting solid mass are linked with the reaction rate and, consequently, the degree of oxidation $u(t)$. Combining equations (4) and (6) results in equations (14)-(16) for the temporal change of the mass of the iron oxide/iron pellet $m(t)$ as well as the temporal molar quantities of iron ($n_{\text{Fe}}(t)$) and magnetite ($n_{\text{Fe}_3\text{O}_4}(t)$), respectively.

$$m(t) = m_{\text{R}} \left(1 - \frac{2M_{\text{O}_2}}{M_{\text{Fe}_3\text{O}_4}} (1 - u(t)) \right) \quad (14)$$

$$n_{\text{Fe}}(t) = (1 - u(t)) \frac{3m_{\text{R}}}{M_{\text{Fe}_3\text{O}_4}} \quad (15)$$

$$n_{\text{Fe}_3\text{O}_4}(t) = u(t) \frac{m_{\text{R}}}{M_{\text{Fe}_3\text{O}_4}} \quad (16)$$

In the previous equations, m_{R} is the initial active mass of the reacting pellet without the stabilizer mass ($m_{\text{R}} = m_0 - m_{\text{st}}$), M_{O_2} represents the molar mass of oxygen, and $M_{\text{Fe}_3\text{O}_4}$ the molar mass of magnetite. Variation in gas stream composition as a result of the respective reaction can be derived from the amount of hydrogen or steam consumed. According to the stoichiometric coefficients (see equations (2)-(3)), the converted molar flow of hydrogen $\Delta \dot{n}_{\text{H}_2}$ and steam $\Delta \dot{n}_{\text{H}_2\text{O}}$ are of the same magnitude. The respective converted molar flow correlates with the time derivative of the oxidation fraction and can be expressed by equation (17).

$$\Delta \dot{n}_{\text{H}_2}(t) = -\Delta \dot{n}_{\text{H}_2\text{O}}(t) = \frac{4m_{\text{R}}}{M_{\text{Fe}_3\text{O}_4}} \frac{du(t)}{dt} \quad (17)$$

The output gas flow is estimated by subtracting the respective converted molar flow rate from the input gas flow rate. Based on the solid mass change, the heat of reaction can be estimated. During the endothermic reduction or exothermic oxidation the heat rates are termed as the reaction heat flow $\dot{Q}_{\text{react}}$, which is proportional to the reaction enthalpy and the converted molar flow of the reactive components as defined by equation (18) [23, 29]. The heat flow $\dot{Q}_{\text{react}}$ is considered positive, if the endothermic reduction takes place, and negative during the exothermic oxidation.

$$\begin{aligned} \dot{Q}_{\text{react}}(T_{\text{s}}, t) = & (h_{\text{mol,gas,out}}(T_{\text{s}}(t)) - h_{\text{mol,gas,in}}(T_{\text{s}}(t))) \dot{n}_{\text{gas}} \\ & + (h_{\text{mol,Fe}_3\text{O}_4}(T_{\text{s}}(t)) - 3h_{\text{mol,Fe}}(T_{\text{s}}(t))) \frac{4m_{\text{R}}}{M_{\text{Fe}_3\text{O}_4}} \frac{du(t)}{dt} \end{aligned} \quad (18)$$

First part of equation (18) represents the enthalpy rate of change of the gas stream upon passing over the reacting solid mass at reaction temperature, while the second part describes the solid phase contribution to the heat of reaction with the specific molar enthalpies of iron $h_{\text{mol,Fe}}(T_{\text{s}})$ and magnetite $h_{\text{mol,Fe}_3\text{O}_4}(T_{\text{s}})$ at reaction temperature T_{s} .

2.3. The lumped non-isothermal model

In this section the lumped, non-isothermal model for the illustrated cylindrical pelletized redox reactor in Figure 2 will be introduced. Also for this model, The Biot-number for the unsteady

heat transfer into/from the solid pellets is below 0.1, so that the lumped assumption can be made. As can be observed, the reactor includes a fixed bed bulk with a defined initial total mass m_0 , which is formed by individual spherical pellets, each has the same pellet diameter, with an initial uniform temperature (800 °C for the reduction phase and 600 °C for the oxidation phase).

The model equations include the previously described unsteady mass and species balances as well as the unsteady energy balance for both the solid pellets and the gas phase along with the definition equations for the different encountered heat transfer rates. These include the heat transfer rate to the ambient air and the heat transfer rate between the solid and the gas phases. The thermal resistance of the reactor wall is ignored relative to both conductive thermal resistance through the insulation material and the convective thermal resistance to the ambient air.

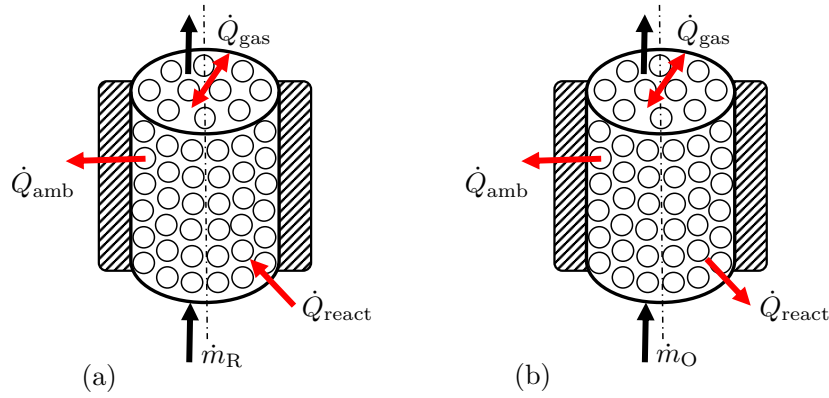


Figure 2. Sketch for the pelletized redox tubular reactor with inlet and outlet streams as a basis for the non-isothermal model for (a) the reduction phase and (b) the oxidation phase.

The temporal reaction heat rate defined by equation (18) is needed for the reacting solid phase during the endothermic reduction reaction and released inside the reacting solid phase during the exothermic oxidation reaction, thus influencing the temporal temperature of the solid phase. Together with the heat rates to the ambient and the rate of heat exchange with the gas phase, the lumped unsteady energy balance for the solid phase is defined by equation (19), from which the temporal course of the solid mass temperature (T_s) is estimated based on the defined initial solid phase temperature.

$$\left(c_{p,\text{mol,Fe}}(T_s(t)) \cdot n_{\text{Fe}}(t) + c_{p,\text{mol,Fe}_3\text{O}_4}(T_s(t)) \cdot n_{\text{Fe}_3\text{O}_4}(t) + c_{p,\text{mass,st}} \cdot x_{\text{st}} \cdot m_0 \right) \frac{dT_s}{dt} = \dot{Q}_{\text{react}}(T_s(t)) - \dot{Q}_{\text{amb,s}}(T_s(t)) + \dot{Q}_{\text{gas}}(T_s(t)) \quad (19)$$

Indeed, equation (19) accounts for the time change of the molar quantities of iron ($n_{\text{Fe}}(t)$) and iron oxide ($n_{\text{Fe}_3\text{O}_4}(t)$) inside the reacting solid phase during each ongoing reaction. The respective molar heat capacities $c_{p,\text{mol}}$ are temperature dependent and are calculated based on the formula defined by the National Institute of Standards and Technology [30]. The third heat capacity term refers to the specific heat of the stabilizer mass, which is an inert mass needed to produce stable iron-oxide pellets, for which a constant mass specific heat capacity $c_{p,\text{mass,st}}$ is assumed.

As explained before, the thermal resistance through the reactor wall is neglected, so that a uniform wall temperature (T_w) is considered in each time step to estimate the respective overall heat flow from the reactor to the ambient air. The total heat flow rate from reactor wall (T_w) to the ambient air (T_{amb}) is expressed by equation (20), with H defining the height and D

the internal diameter of the tubular pelletized reactor [22].

$$\dot{Q}_{\text{amb}}(T_w(t)) = \frac{\pi \cdot H \cdot (T_w - T_{\text{amb}})}{\frac{1}{2k_{\text{iso}}(T_w(t))} \ln \frac{D+2\delta_{\text{iso}}}{D} + \frac{1}{h_{\text{amb}} \cdot (D+2\delta_{\text{iso}})}} \quad (20)$$

According to the homogenized bulk model of solid and gas, the heat transfer to the ambient can be divided between both phases depending on the bulk porosity. In other words, the instantaneous wall temperature ($T_w(t)$) in equation (20), is averaged between the instantaneous temperatures of the gas and solid phases based on the bulk porosity. Equation (21) describes the part of the total ambient heat rate, which is lost by the solid phase, which appears as the second term on the right hand side of equation (19).

$$\dot{Q}_{\text{amb,s}}(T_s(t)) = \frac{\pi \cdot H \cdot (1 - \epsilon_{\text{bed}})(T_s(t) - T_{\text{amb}})}{\frac{1}{2k_{\text{iso}}(T_w(t))} \ln \frac{D+2\delta_{\text{iso}}}{D} + \frac{1}{h_{\text{amb}} \cdot (D+2\delta_{\text{iso}})}} \quad (21)$$

For the energy balance of the gas phase (equation (29)), the part of the ambient heat loss rate from the gas phase is defined by equation (22).

$$\dot{Q}_{\text{amb,g}}(T_{\text{gas}}(t)) = \frac{\pi \cdot H \cdot \epsilon_{\text{bed}}(T_{\text{gas}}(t) - T_{\text{amb}})}{\frac{1}{2k_{\text{iso}}(T_w(t))} \ln \frac{D+2\delta_{\text{iso}}}{D} + \frac{1}{h_{\text{amb}} \cdot (D+2\delta_{\text{iso}})}} \quad (22)$$

The external convective heat transfer to the ambient air is described by a constant heat transfer coefficient h_{amb} of $10 \text{ W}/(\text{m}^2\text{K})$ [31]. To reduce the heat losses, a thermal insulation having a thermal conductivity k_{iso} and a thickness of δ_{iso} is considered. As the temperature changes between a minimum of 270°C and a maximum of 840°C during the overall process, the temperature dependency of the thermal conductivity is considered by equation (23). The temperature of the insulation layer is assumed to equal the average value between the instantaneous wall and the ambient temperatures. [32].

$$k_{\text{iso}}(T_w(t)) = 0.0328 \cdot \exp\left(0.0032 \cdot \frac{T_{\text{amb}} + T_w(t)}{2}\right) \quad (23)$$

The convective heat transfer rate between the gas and the solid phases is determined by equation (24) applying the total heat transfer area within the fixed bed, derived from the volume-specific surface area of the assumed spherical pellets (equation (25)), [32] and the Nusselt-Correlation (equation (26)), [33].

$$\dot{Q}_{\text{gas}}(T_{\text{gas}}(t), T_s(t)) = \frac{k_{\text{gas}}(T_{\text{gas}}(t))}{d_p} \cdot Nu \cdot A_{\text{trans}} \cdot (T_{\text{gas}}(t) - T_s(t)) \quad (24)$$

$$A_{\text{trans}} = \frac{6m_0}{\rho_s \cdot d_p} \quad (25)$$

$$Nu = 3.22 \cdot (Re \cdot Pr)^{\frac{1}{3}} + 0.117 \cdot Re^{0.8} \cdot Pr^{0.4} \quad (26)$$

The applied temperature difference in equation (24) determines a positive heat flow for the solid material and a negative one for the gas flow, if the gas temperature is higher than the solid phase temperature, and vice versa. Further material properties of the solid phase are the pellet diameter d_p , the solid bulk density ρ_s and the total initial mass of the solid material m_0 . Relevant fluid properties are the thermal conductivity k_{gas} , the Prandtl number Pr and the Reynolds number Re of the gas flow.

The Reynolds number of the gas flow is calculated by equation (27), with the density ρ_{gas} and the dynamic viscosity η_{gas} . The flow velocity u_0 of the gas stream is expressed by equation (28), where $c_{\text{mol,gas}}$ represents the molar concentration of the gas stream [34].

$$Re = \frac{d_p \cdot u_0 \cdot \rho_{\text{gas}}(T_{\text{gas}}(t))}{\eta_{\text{gas}}(T_{\text{gas}}(t))} \quad (27)$$

$$u_0 = \frac{\dot{n}_{\text{gas}}(T_{\text{gas}}(t))}{c_{\text{mol,gas}}(T_{\text{gas}}(t)) \cdot \frac{\pi}{4} D^2} \quad (28)$$

The energy balance of the gas stream accounts for the heat loss rates to the solid phase and to the ambient air and is described by equation (29). In this equation, the instantaneous gas outlet temperature $T_{\text{gas,out}}$ is estimated from the model input temperature $T_{\text{gas,in}}$, the molar flow rate $\dot{n}_{\text{gas}}$ of the gas stream and its molar specific heat capacity $c_{\text{p,mol,gas}}$.

$$T_{\text{gas,out}}(t) = T_{\text{gas,in}} - \frac{\dot{Q}_{\text{gas}} + \dot{Q}_{\text{amb,g}}}{c_{\text{p,mol,gas}}(T_{\text{gas}}(t)) \cdot \dot{n}_{\text{gas}}} \quad (29)$$

Because of the lumped model assumption, the temperature-dependent material characteristics as well as the relevant gas heat flows are estimated based on an average gas temperature between the input and output gas streams. Table 4 presents the setup values for the non-isothermal model parameters, while Table 5 depicts the initial values of the state variables as well as the tested operating conditions, whose results will be presented and discussed in the coming section.

Table 4. Applied parameters for the non-isothermal model.

Symbol	Description	Value
A_{trans}	Internal heat transfer area	0.464 m ²
D	Internal diameter of reactor	0.075 m
H	Height of reactor	0.21 m
h_{amb}	External heat transfer to ambient	10 W/(m ² K)
m_{R}	Initial active mass of the reacting pellets	2 kg
p	Reactor pressure	1.013 bar
T_{amb}	Ambient temperature	20 °C
δ_{iso}	Thickness of thermal insulation	0.05 m
ρ_{s}	Solid bulk density	2150 kg/m ³
ϵ_{bed}	Bulk porosity	0.36
d_{p}	Single pellet diameter	0.012 m
ρ_{p}	Single pellet density	3350 kg/m ³
$c_{\text{p, mass, st}}$	Specific heat capacity of stabilizer mass	0.68 kJ/(kgK)
x_{st}	Stabilizer mass fraction	0.115

Table 5. Initial values of the state variables and the tested operating conditions for the depicted non-isothermal reactor in Figure 2.

Symbol	Description	Value		Unit
		Reduction	Oxidation	
$u(t=0)$	Oxidation fraction	1	0	-
$\dot{n}_{\text{gas,in}}$	Input mole flow (gas phase)	0.1	0.1	kmol/h
		300	300	°C
$T_{\text{gas,in}}$	Input temperature (gas phase)	500	500	°C
		700	700	°C
$x_{\text{H}_2,\text{in}}$	Input hydrogen mole fraction	0.8	-	-
$x_{\text{H}_2\text{O},\text{in}}$	Input steam mole fraction	-	0.8	-
$x_{\text{N}_2,\text{in}}$	Input nitrogen mole fraction	0.2	0.2	-
$m(t=0)$	Solid mass	2.0	1.51	kg
$T_{\text{s}}(t=0)$	Fixed bed temperature (solid phase)	800	600	°C

2.4. Simulation tool

In the field of process engineering, AspenTech provides suitable applications for analyzing and simulating chemical processes. Especially for dynamic applications, the software Aspen Custom Modeler (ACM) is used, as it has an efficient implicit solution algorithm for time-dependent ordinary differential equations [35]. Furthermore, models can be extrapolated

with a moderate effort and can be interconnected with further processes. For these reasons, the lumped isothermal and non-isothermal models are developed in ACM. In addition to the efficient numerical solution of the developed reactor model, ACM includes a large material database for gases and solids. Variables related to the investigated pellet, which represents the solid phase, are only part of the reactor model, whereas the gas phase is described by a material stream.

The material properties of the gas stream, which contains H_2 or H_2O and N_2 , are determined by the Aspen Properties database [36]. Input data include the material stream's variables of state, like temperature, pressure, and molar composition, which are predefined for the input stream or calculated within the model for the exit stream.

Since in our application, iron is not part of the gas stream, but of the reactor bulk, the molar enthalpy h_{mol} and the molar heat capacity $c_{p,mol}$ of the solid components Fe_3O_4 and Fe have to be integrated in the reactor model for the calculation of the heat flow and the thermal behavior of the solid material. To this aim, the empirically determined polynomial functions for enthalpy and molar heat capacity according to equation (30) and equation (31), respectively, based on the National Institute of Standards and Technology [30] are used.

$$h_{mol}(T) = A \frac{T}{1000} + \frac{B}{2} \left(\frac{T}{1000} \right)^2 + \frac{C}{3} \left(\frac{T}{1000} \right)^3 + \frac{D}{4} \left(\frac{T}{1000} \right)^4 - E \frac{T}{1000} + F \quad (30)$$

$$c_{p,mol}(T) = A + B \frac{T}{1000} + C \left(\frac{T}{1000} \right)^2 + D \left(\frac{T}{1000} \right)^3 + \frac{E}{\left(\frac{T}{1000} \right)^2} \quad (31)$$

In both equations, T stays for the absolute temperature in K, while A to F stay for the correlation coefficients, which are defined in Table 6.

Table 6. Correlation coefficients of the molar enthalpy function of Fe and Fe_3O_4 based on the National Institute of Standards and Technology [30].

	A	B	C	D	E	F
Fe						
$T < 700\text{K}$	18.42868	24.64301	-8.91372	9.664706	-0.012643	-6.573022
$700\text{K} \leq T < 1042\text{K}$	-57767.65	137919.7	-122773.2	38682.42	3993.08	24078.67
$1042\text{K} \leq T < 1100\text{K}$	-325.8859	28.92876	0	0	411.9629	745.8231
$T \geq 1100\text{K}$	-776.7387	919.4005	-383.7184	57.08148	242.1369	697.6234
Fe_3O_4						
$T < 900\text{K}$	104.2096	178.5108	10.6151	1.132534	-0.994202	-1163.336
$T \geq 900\text{K}$	200.8320	1.586435×10^{-7}	-6.661682×10^{-8}	9.452452×10^{-9}	3.18602×10^{-8}	-1174.135

Figure 3 illustrates a flowchart of the interacting model segments, including the equations and the key variables, which are exchanged between them. The input gas stream defines the gas phase composition and triggers the reduction or oxidation (see equation (13)). Out of the respective dominant reaction (see equations (5)-(6)), and the kinetic set of equations (8)-(12), the differential oxidation fraction of the reaction mass is estimated. The next step is to calculate the temporal mass change of the solid phase and its molar quantities (see equations (14)-(16)) along with the changes in molar gas phase flow rate (see equation (17)). Finally, the respective energy balance for the isothermal or the non-isothermal reaction is applied to determine the temporal change of the solid material and, consequently, the solid and gas phase temperatures. The last step is to determine the heat rate of reaction, along with the heat loss and the gas-solid heat exchange rates (see equations (18)-(29)).

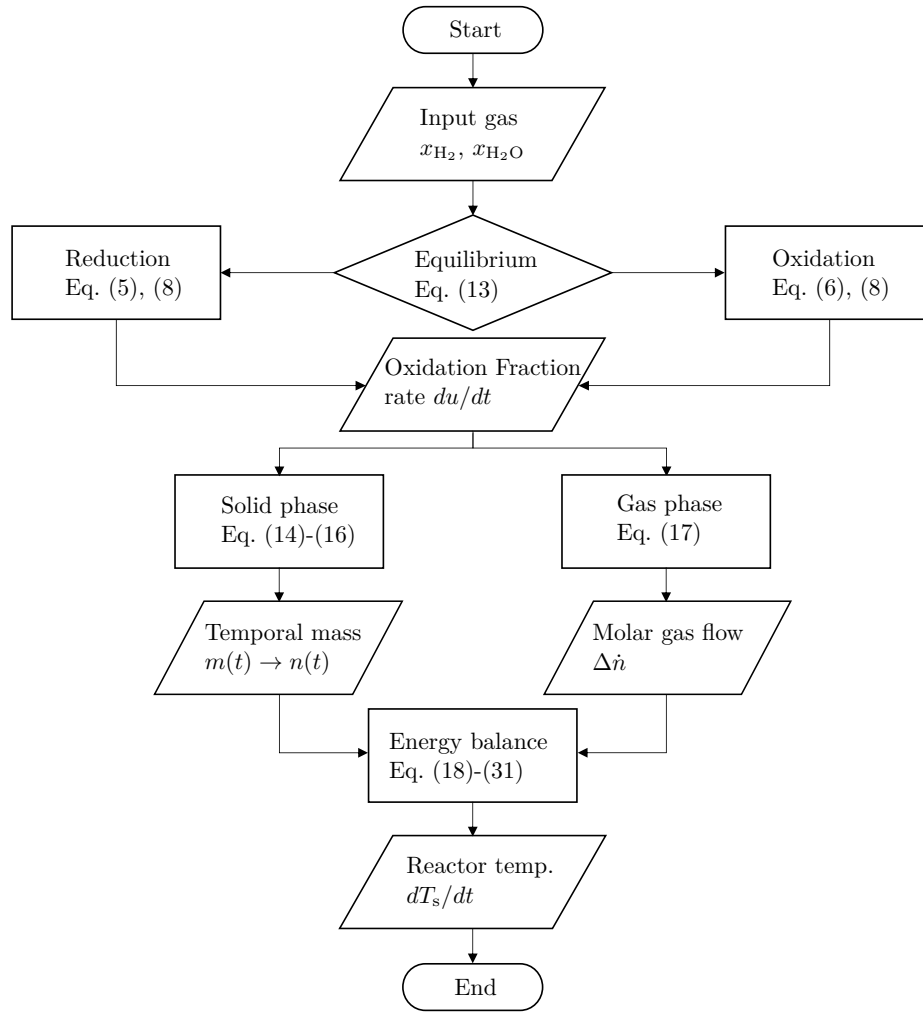


Figure 3. Flow chart of redox simulation process in ACM with interacting model parts and the key variables.

3. Results

To validate the developed isothermal model, the simulated conversion rates $\alpha(t)$ (equations (8)-(12)) will be first compared with the experimentally obtained data [20]. In addition, the simulation results of the isothermal storage process on a single pellet as well as the heat flow rates (equation (18)) consumed during the endothermic reduction or released during the exothermic oxidation are presented and discussed in the following sub-sections. The isothermal storage process has been measured and simulated at the reaction temperature of $T = 700\text{ }^{\circ}\text{C}$ and a continuous input gas molar concentration of 80% (condition ro₃ in Table 2) for both reduction (charging) and oxidation (discharging) phases.

The absolute deviation (AD) between the experimentally measured reduction/oxidation conversion rates α_{Exp} and the modeled values α_{Fit} , is defined by equation (32). For a better interpretation of the results, we decided to express AD in [%].

$$\text{AD} = |\alpha_{\text{Exp}} - \alpha_{\text{Fit}}| \cdot 100\% \quad (32)$$

In the third part of this section, the necessary heat flow rates to be added or rejected from the single pellet during the isothermal reduction and oxidation phases, respectively, are estimated. Moreover, the obtained results from the non-isothermal model for a single reactor having the listed parameters in Table 4 under the initial and operating conditions defined in Table 5 will be presented and discussed. Finally, five of such non-isothermal reactors

will be connected in series and simulated to elaborate the influence of the variable input gas temperature and concentration on the temporal reactive performance of the included storage mass in each reactor.

3.1. Isothermal conversion rates

Figure 4(a) illustrates the temporal experimental and modeled reduction fractions obtained with the hydrogen gas concentration condition ro_1 in the input gas stream (in total 250 ml/min) at the isothermal conditions of 600 °C, 700 °C and 800 °C (see Table 2). Increasing the reaction temperature from 600 °C to 700 °C leads to an acceleration of 68% for reaching a reduction fraction of $\alpha_{Re} = 0.8$, as the needed time duration is reduced from 134 to 43 min. The further enhancement of the reaction temperature to 800 °C results in an additional acceleration of the reduction reaction by 47% as the time needed is decreased from 43 to 23 min. It can be concluded that the reduction reaction gets faster with increasing the reaction temperature. Such a result is in phase with the results obtained by [37–39] for such an endothermic reaction. In addition, the curves in Figure 4 present the corresponding absolute deviations (AD) between the measured and simulated values according to equation (32). A very good agreement has been obtained between the experimental data and the modeled results with a maximum deviation of 3.1% at 600 °C.

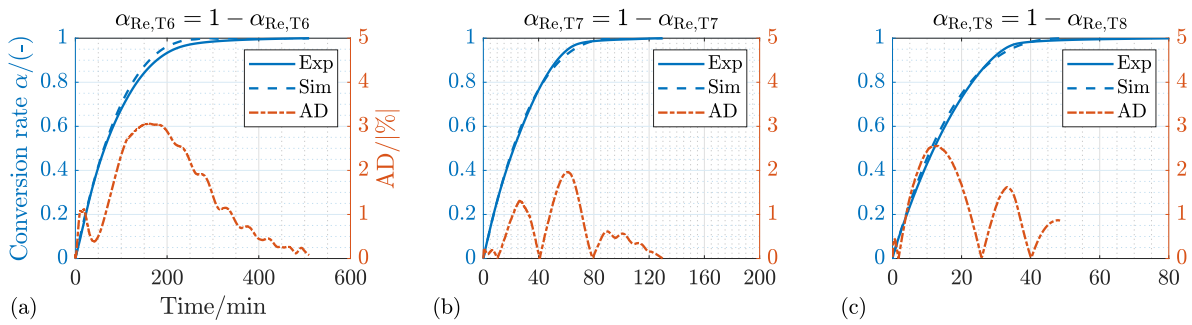


Figure 4. Temporal experimental reduction fractions of the sample (solid lines) compared to the ASPEN simulation model (dash lines) for the input gas concentration ro_2 (see Table 2) and the corresponding absolute deviations (dash dot line) between experiment and simulation according to equation (32); Reaction temperature (a) T6 = 600 °C; (b) T7 = 700 °C; (c) T8 = 800 °C

The concentration dependency of the reduction conversion rates is depicted in Figure 5 at the reaction temperature of 700 °C and an increasing H_2 gas concentration from ro_1 to ro_3 (Table 2). The time needed to achieve a reduction conversion rate of 80% of the maximum possible mass change ($\alpha_{Re} = 0.8$) decreases from 160 min down to 45 min (an acceleration of 72%) as the H_2 -concentration in the reactive gas mixture increases from 25% to 80%. A similar result is reported on in the study of [39]. In addition, the dash-dotted curves in Figure 5(b) represent the respective deviation between the measured and modeled values according to equation (32). The obtained maximum deviation of 2.4% at ro_2 demonstrates an excellent agreement between the modeled and experimental values.

The model validation for the oxidation reactions at different temperatures and the steam molar concentration of 33% is presented in Figure 6, while Figure 7 illustrates the concentration influence on the oxidation reaction kinetics at 700 °C. The graphs in Figure 6 demonstrate an acceleration of the oxidation reaction kinetics with the reaction temperature increase, an in phase result with those obtained by [40,41]. Increasing the sample temperature from 600 °C to 700 °C results in decreasing the time needed for the oxidation fraction to reach $\alpha_{Ox} = 0.8$ from 41 to 35 min (a kinetic acceleration of 15%). Further enhancing the temperature to 800 °C accelerates the oxidation kinetics by another 16%, as the required time to reach a fraction of $\alpha_{Ox} = 0.8$ is reduced to 27 min. The maximum deviation between experiment and simulation

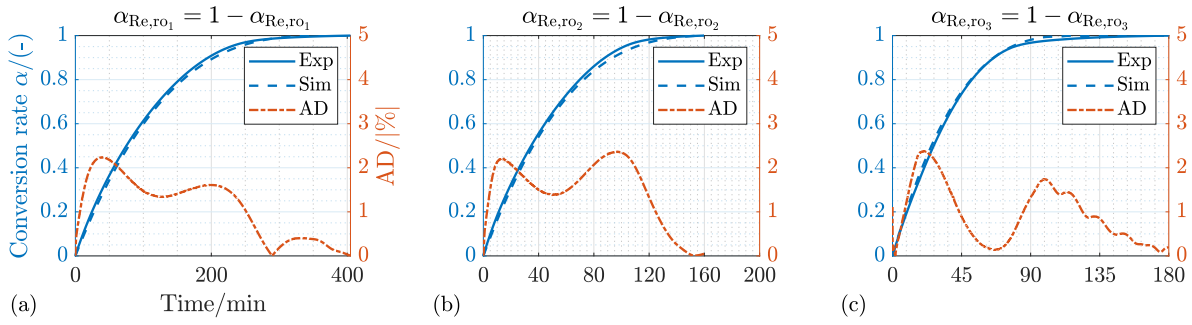


Figure 5. Temporal experimental reduction fractions of the sample (solid lines) compared to the ASPEN simulation model (dash lines) at the reaction temperature $T = 700\text{ }^{\circ}\text{C}$ and the corresponding absolute deviations (dash dot line) between experiment and simulation according to equation (32); Input gas concentration (a) ro_1 ; (b) ro_2 ; (c) ro_3 (see Table 2).

amounts to 4.6% at the reaction temperature of $600\text{ }^{\circ}\text{C}$, which demonstrates a very good agreement.

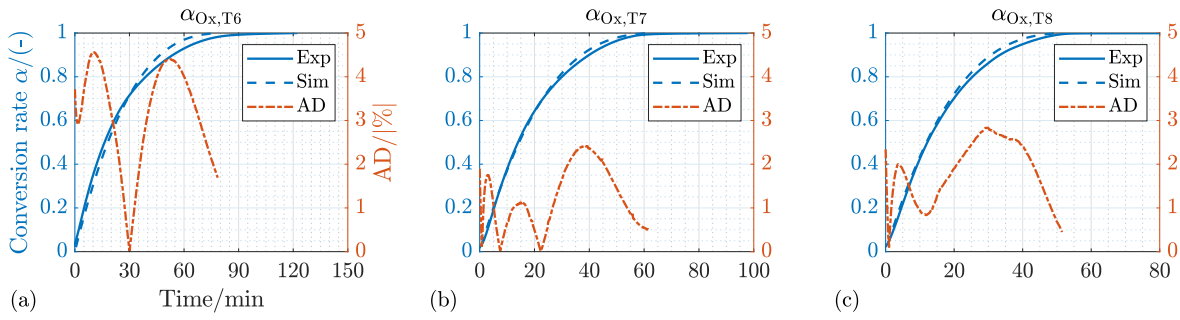


Figure 6. Temporal experimental oxidation fractions of the sample (solid lines) compared to the ASPEN simulation model (dash lines) for the gas concentration ro_1 (see Table 2) and the corresponding absolute deviations (dash dot line) between experiment and simulation according to equation (32); Reaction temperature (a) $T6 = 600\text{ }^{\circ}\text{C}$; (b) $T7 = 700\text{ }^{\circ}\text{C}$; (c) $T8 = 800\text{ }^{\circ}\text{C}$.

The illustrated results in Figure 7 demonstrate a higher oxidation kinetics with increasing the steam concentration in the reacting gas flow. The time needed to achieve a conversion ration of $\alpha_{Ox} = 0.8$ decreases by 36%, from 44 min to 28 min as the H_2O -concentration in the gas mixture increases from 33% to 80%. The maximum deviation between the modeled and experimental data amounts to 4.0%, which implies that the concentration dependency of the oxidation kinetics can be reproduced quite precisely with the introduced model.

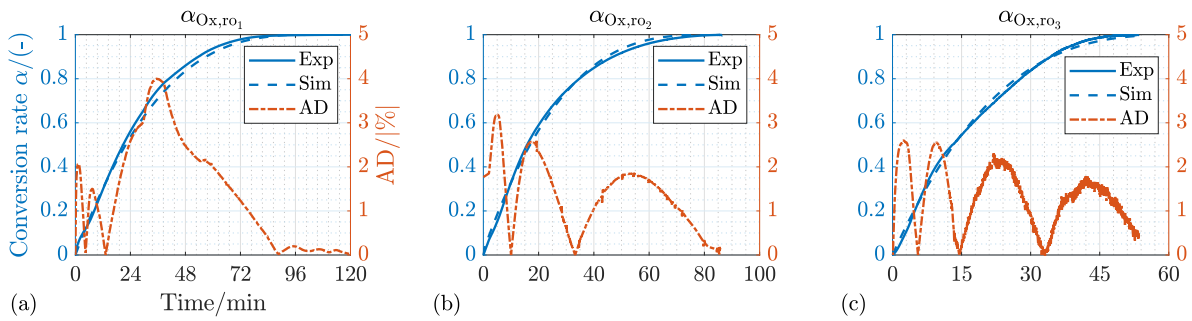


Figure 7. Temporal experimental oxidation fractions of the sample (solid lines) compared to the ASPEN simulation model (dashed lines) at the reaction temperature $T = 700\text{ }^{\circ}\text{C}$ and the corresponding absolute deviations (dash dot line) between experiment and simulation according to equation (32); Input gas concentration (a) ro_1 ; (b) ro_2 ; (c) ro_3 (see Table 2).

3.2. Isothermal storage process

As explained before, the developed isothermal model is applied to analyze an isothermal storage process, which includes consecutive reduction and oxidation phases with a holding phase in between. The chosen parameters for the storage process are $T = 700\text{ }^{\circ}\text{C}$ as reaction temperature and the gas molar concentration of 80% (condition ro₃ in Table 2) for both reduction (charging) and oxidation (discharging) phases. The duration of the holding (storage) phase has been set to 117 min. Such isothermal storage process has been experimentally investigated with a single iron-oxide pellet inside our STA device. Both experimental and simulated temporal mass changes of the sample $m(t)$ as well as the absolute deviation between them are depicted in Figure 8(a). For both measured and modeled storage processes, the reduction phase takes about 123 min. After the given holding phase of 117 min, the consecutive oxidation phase takes about 55 min.

The initial sample mass $m_0 = 3589\text{ mg}$ decreases with time by $\Delta m_{\text{react}} = 890\text{ mg}$ during reduction and increased by the same amount during oxidation, which is equivalent to the mass of oxygen removed/gained during the reduction/oxidation reactions, respectively. Based on the presented absolute deviations in Figure 8(a), the measured storage process could be reproduced extraordinarily well with a maximum deviation of 1.5% by the introduced simulation model.

The simulated temporal change of the solid molar quantity $n_{\text{Fe}_3\text{O}_4}$ per kg of the initial sample mass m_0 as well as the temporal converted molar flow of the reactive gas streams are presented in Figure 8(b). Since Fe_3O_4 is converted to Fe during the reduction phase, its molar quantity decreases with time until the complete conversion is realized. During the oxidation phase, the reverse process takes place and the initial molar quantity of Fe_3O_4 is retained at the end of the oxidation phase. The absolute change in mass is coherent with the initial mass of the raw iron oxide material m_0 . Related to its initial mass, 3.87 mol/kg magnetite are converted to 11.61 mol/kg iron during the reduction phase and vice versa during the oxidation phase (see Figure 8(b)).

According to the identical stoichiometric coefficients of H_2 and H_2O within the modeled redox reaction, the consumed H_2 equals the produced H_2O and vice versa. This implies that the area below both orange curves representing the converted molar flow rates of both gases are equal. At the beginning of each reaction, the conversion rate attains its maximum value as the driving force for both diffusion and reaction is at its maximum value. Such conversion rates approach zero at the end of each phase as the equilibrium states are approached. Due to the higher kinetics of the oxidation process, its peak value of the converted molar flow rate of steam into hydrogen of 0.162 mol/h is higher than the peak value of the converted rate of hydrogen into steam of 0.07 mol/h at the beginning of the reduction phase.

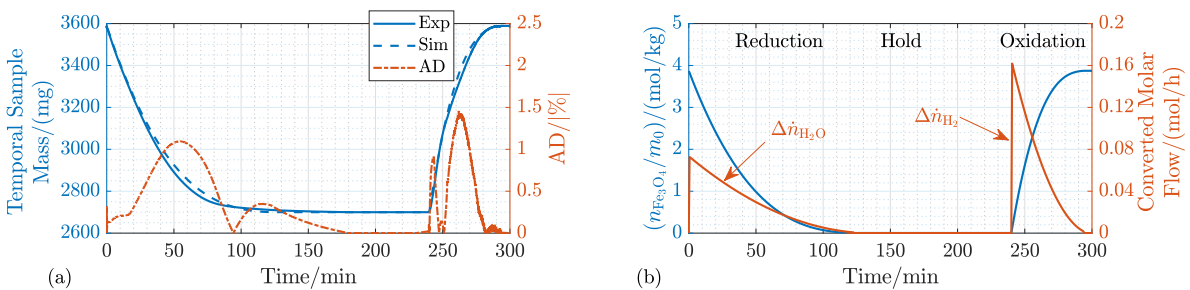


Figure 8. Consecutive reduction, holding and oxidation phase at $T = 700\text{ }^{\circ}\text{C}$, $x_{\text{H}_2,\text{in}} = x_{\text{H}_2\text{O},\text{in}} = \text{ro}_3$; (a) Temporal experimental reaction fraction of sample mass m_0 (solid line) compared to ASPEN simulation model (dash line) with its absolute deviation (dash dot line); (b) Molar quantity of the solid material and converted gas flow based on equations (16)-(17).

3.3. Isothermal heat flow rates

Based on the energy balance formulated with equation (18) along with the necessary temporal variables and parameters out of the isothermal model equations, the temporal heat rates required to be added to realize the isothermal endothermic reduction or rejected to maintain the isothermal exothermic oxidation reaction conditions in our STA device are estimated. Figures 9 and 10 depict the obtained reaction heat rates together with the respective conversion rates at different reaction conditions for both reduction and oxidation phases, respectively. For better comparability, the heat flow rates are illustrated as mass specific quantities related to the initial sample mass m_0 as expressed in the following equation.

$$\dot{q}_{R/O} = \frac{\dot{Q}_{\text{react}}}{m_0} \quad (33)$$

Figure 9(a) presents the obtained results for the isothermal reduction at 700 °C and the input gas molar H_2 -concentrations of 50% and 80%, while Figure 9(b) illustrates the same results at the input gas molar concentration of $x_{H_2, \text{in}} = 50\%$ at the reaction temperatures of 600 °C and 800 °C. Respective temporal trends of the conversion rates are in correlation with the previously presented reaction kinetics (see Section 3.1).

At the beginning of each reaction and because of the valid non-equilibrium state, the time derivative of the oxidation fraction is maximum, and correspondingly, the reaction heat rate attains its peak value, which decays with the progress of the reaction and vanishes as the equilibrium state at the end of each reaction is reached. As the reduction kinetics increases with increasing the hydrogen concentration in the educt gas stream, the peak of the mass specific heat rate increases from $\dot{q}_{R, rO_2} = 110 \text{ W/kg}$ to $\dot{q}_{R, rO_3} = 156 \text{ W/kg}$ as the hydrogen molar concentration increases from 50% to 80% as depicted in Figure 9(a). Increasing the reaction temperature from 600 °C to 800 °C results in enhancing the peak of the mass specific heat flow rate from $\dot{q}_{R, T6} = 52 \text{ W/kg}$ to $\dot{q}_{R, T8} = 218 \text{ W/kg}$ (see Figure 9(b)).

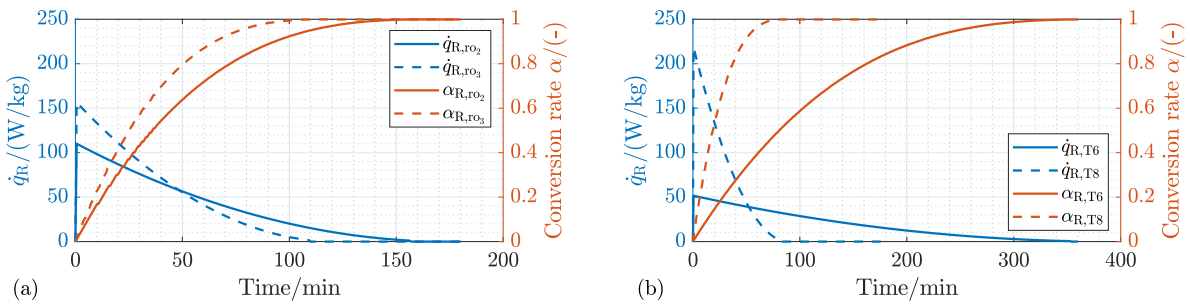


Figure 9. Calculated mass specific heat flow rates ($\dot{q}_R$), based on equation (33) and the corresponding conversion rates (α_R) at different reduction conditions; (a) Reaction temperature of $T = 700^\circ\text{C}$ at the varied input gas concentration of $x_{H_2, \text{in}} = rO_2$ and $x_{H_2, \text{in}} = rO_3$ (see Table 2); (b) Input gas concentration of $x_{H_2, \text{in}} = rO_2$ with reaction temperatures $T6 = 600^\circ\text{C}$, $T8 = 800^\circ\text{C}$.

Figure 10 presents the estimated mass specific heat flow rates at different input gas molar concentrations and temperatures for the oxidation reaction. The modeled peak values of the mass specific heat flow rates increases from $|\dot{q}_{O, rO_2}| = 219 \text{ W/kg}$ to $|\dot{q}_{O, rO_3}| = 311 \text{ W/kg}$ as the molar concentration of steam in the reacting gas increases from 50% to 80% as illustrated in Figure 10(a). Increasing the oxidation reaction temperature from 600 °C to 800 °C is associated with enhancing the mass specific peak heat flow rate from $|\dot{q}_{O, T6}| = 183 \text{ W/kg}$ to $|\dot{q}_{O, T8}| = 271 \text{ W/kg}$ as presented in Figure 10(b).

Indeed, for the modeled isothermal redox reactions of iron oxide/iron, the integral heat of both reduction and oxidation should be equal at each isothermal condition. Strictly speaking, the integral mass specific reaction energy, which is needed to be delivered to or rejected from

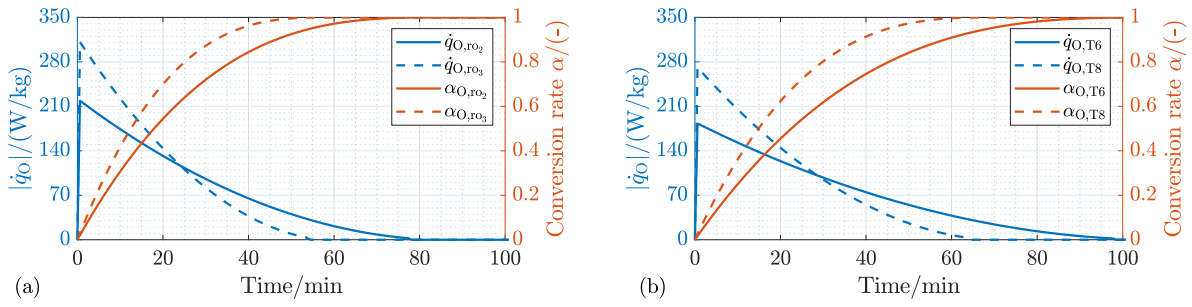


Figure 10. Calculated mass specific heat flow rates ($\dot{q}_O$), based on equation (33) and the corresponding conversion rates (α_O) at different oxidation conditions; (a) Reaction temperature of $T = 700$ °C with varied input gas concentration of $x_{H_2O,in} = ro_2$ and $x_{H_2,in} = ro_3$ (see Table 2); (b) Input gas concentration of $x_{H_2O,in} = ro_2$ at the reaction temperatures $T_6 = 600$ °C and $T_8 = 800$ °C.

the sample mass in order to maintain the isothermal conditions, does vary from 404 kJ/kg at 600 °C to 395 kJ/kg at 800 °C.

3.4. Non-isothermal results

The modeled, non-isothermal, pelletized cylindrical reactor contains a total mass of $m_0 = 2$ kg. This mass includes a stabilizer mass fraction of $x_{st} = 0.115$ with a stabilizer constant specific heat capacity of $c_{p,mass,st} = 0.68$ kJ/(kgK). To reduce heat transfer to the ambient, a thermal insulation with a thickness of $\delta_{iso} = 0.05$ m is applied. The input gas molar flow rate for all simulations within this section is set to $\dot{n}_{gas} = 0.1$ kmol/h. Based on the defined model parameters in Table 4, the non-isothermal reactor model has been simulated under the initial values of the state variables and the operating conditions listed in Table 5.

Figure 11(a) presents the temporal trend of the solid material temperature for the charging or reduction phase under fixed gas stream input temperatures of 300 °C, 500 °C and 700 °C. As the reduction reaction is endothermic, the solid mass temperature starts to decrease from the initial temperature of 800 °C, as the reduction reaction proceeds. As the input gas temperature is lower than the initial solid temperature, the solid phase heats up the gas stream until its temperature falls below the gas temperature. Based on the depicted results in Figure 11(a), this is only the case with the gas inlet temperature of 700 °C, with the related curve showing a reversed trend for the solid phase temperature, indicating a sufficient heat flow rate from the gas phase into the solid phase after almost 60 min. For the two lower input gas stream temperatures, the heat rate of reaction is higher than the heat transfer rate from the gas phase and both seem to be equal after 150 min, where the solid phase temperature remains almost constant with time. Strictly speaking, $T_s(t > 150 \text{ min})$ amounts to 427 °C for the input gas temperature of 500 °C and 267 °C for the input gas temperature of 300 °C.

Figure 11(b) illustrates the corresponding conversion rates $\alpha(t)$. It is obvious, that, only the higher gas temperature ($T_{gas,in} = 700$ °C) leads to an almost complete conversion within the considered reduction time interval of 360 min. The explained reduction of the solid phase temperature under the other two input gas stream temperatures, results in a significant reduction of the reaction kinetics and limits, therefore, the reachable conversion rate. For example, at an input gas temperature of $T_{gas,in} = 500$ °C, the conversion rate reaches only 0.45 after 250 min. It is also quite obvious, that an input gas stream temperature of 300 °C is too low, as the corresponding conversion rate can't go higher than 0.23 after 360 min. It can, moreover, be concluded that the temperature of the input gas stream, for the tested operating condition, should be at least 700 °C, in order to accomplish the reduction phase withing 6 h, or the reaction duration must be extensively prolonged.

The transferred or evolved heat flow rates during the non-isothermal reduction phase are

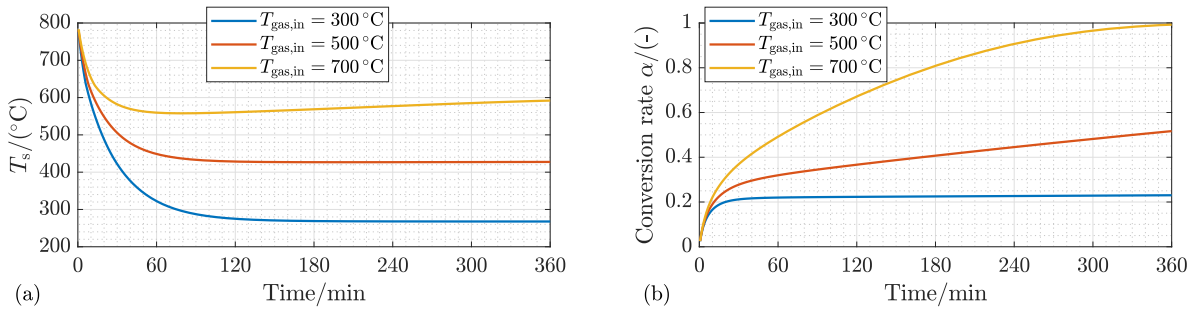


Figure 11. (a) Temporal trend of the solid material temperature and (b) the related conversion rates at different input gas temperatures of 300 °C, 500 °C and 700 °C for the reduction process.

presented in Figure 12. Figure 12(a) depicts the overall heat transfer rate received by the ambient air $\dot{Q}_{amb}$, which decreases with time as the temperature of the solid phase inside the reactor follows the trends presented in Figure 11(a). As the main driving force for this heat rate is the temperature difference between the temporal reactor wall temperature and the fixed ambient temperature, the trend of the ambient heat flow rates do follow the trend of the solid phase temperatures depicted in Figure 11(a).

As described previously, the reduction kinetics and, correspondingly, the respective heat of reaction $\dot{Q}_{react}$ are strongly temperature dependent, which can be also seen in Figure 12(b). Because of the identical initial reactor temperature of all three considered cases, every initial heat of reaction equals $\dot{Q}_{react}(0\text{ min}) = -0.53\text{ kJ/s}$. The lower the input gas temperature the more distinctive is the temperature reduction of the solid material and, therefore, the decline of the reaction heat flow rate. The exchanged heat flow rate between the gas and solid phases, depicted in Figure 12(c), describes the amount of heating power transferred from the gas phase into the solid phase, which must be negative in case the gas temperature is lower than the solid phase temperature and vice versa. According to the presented data in Figure 12(c), the transition from negative to positive heat flow rates takes place after 8, 39 and 85 min for the input gas temperatures of 700 °C, 500 °C and 300 °C, respectively. In case of the lowest considered gas input temperature of 300 °C the gas phase mainly cools down the solid phase, the magnitude of the exchanged heat rate increases from about $\dot{Q}_{gas,300\text{ °C}}(0\text{ min}) = -0.48\text{ kJ/s}$ to $\dot{Q}_{gas,300\text{ °C}}(360\text{ min}) = 0.02\text{ kJ/s}$. In contrast to this case, the gas input temperature of 700 °C shows a cooling effect to the solid phase only over the first 8 min and then shows a heating effect on the solid phase with a maximum of $\dot{Q}_{gas,700\text{ °C}}(78\text{ min}) = 0.1\text{ kJ/s}$, which falls down to $\dot{Q}_{gas,700\text{ °C}}(360\text{ min}) = 0.07\text{ kJ/s}$.

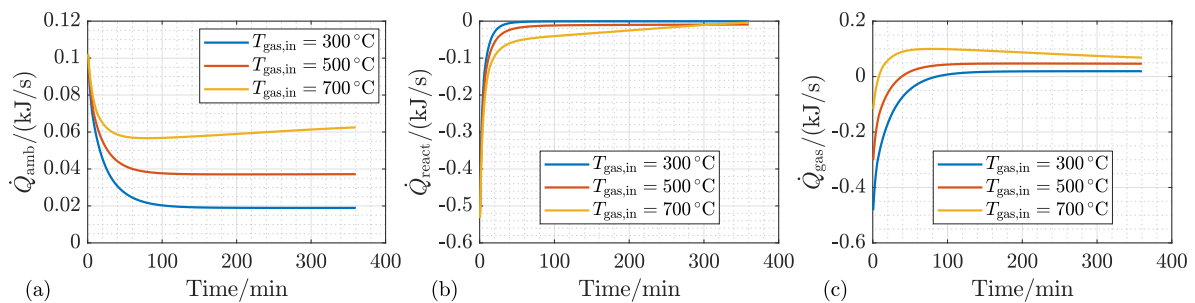


Figure 12. Temporal trend of the heat flow rates associated with the reduction phase at the input gas temperatures of 300 °C, 500 °C and 700 °C; (a) Heat transfer rate received by the ambient $\dot{Q}_{amb}$; (b) Heat rate of reaction $\dot{Q}_{react}$; (c) Exchanged heat between the gas and solid phases $\dot{Q}_{gas}$.

As initial conditions for the oxidation reaction, the conversion rate is set to $\alpha(0\text{ min}) = 0$ and an initial temperature of the solid phase $T_s(0\text{ min}) = 600\text{ °C}$ is considered. The temporal

trends of the solid material temperatures at the different gas stream input temperatures $T_{\text{gas,in}}$ of 300 °C, 500 °C and 700 °C are depicted in Figure 13(a). In contrast to the reduction reactions, the exothermic nature of the oxidation reactions results in evolving the heat of reaction inside the solid phase, thus enhancing its temperature with time. The higher the temperature of the input gas stream, the lower is the chance to get the solid phase being cooled down by the gas stream. Accordingly, the solid phase shall exhibit a temperature increase with time, unless the gas temperature is adequately low. In case of an input temperature of 700 °C, the solid mass overheats rapidly up to $T_s(22 \text{ min}) = 837$ °C. Due to the higher solid phase temperature, the reaction rate is enhanced, so that the solid phase is converted entirely within 50 min and reaches then a temperature of 698 °C. The realized faster kinetics are associated, however, with the danger of the migration of the iron ions towards the surface of the pellets (surface sintering above 800 °C [15]), which implies a drastic reduction of the gas diffusion rates with the number of repeated redox cycles until the process cases completely. In practice, such an operation condition shall be avoided, in order to guarantee a long-time stability of the storage process. A lower input gas temperature of 500 °C is associated with a significant cooling effect. Therefore, the overheating of the solid material within the first 17 min of reaction does not exceed $T_s(17 \text{ min}) = 730$ °C and the solid phase temperature reaches about $T_s(75 \text{ min}) = 517$ °C at the end of this oxidation reaction. The lowest input gas stream's temperature of 300 °C allows only a temperature rise to $T_s(10 \text{ min}) = 638$ °C. The associated cooling effect with this low input gas temperature results in reducing the solid phase temperature down to $T_s(90 \text{ min}) = 338$ °C at the end of the considered time interval of 90 min.

The conversion rates $\alpha(t)$ associated with the respective input gas temperatures are presented in Figure 13(b). The higher input temperatures and, consequently, the higher solid phase temperatures lead to an accelerated conversion to $\alpha(t) = 1.0$ after 50 min for the input gas temperature of 700 °C and $\alpha(t) = 1.0$ at 75 min for the input gas temperature of 500 °C, respectively. In case of 300 °C, the realized lower solid phase temperatures entail a deceleration of the reaction kinetics. Accordingly, the conversion rate reaches $\alpha(t) = 0.99$ first after 80 min. In general, the results confirm a less distinctive temperature dependency of the oxidation reaction compared to the reduction reaction.

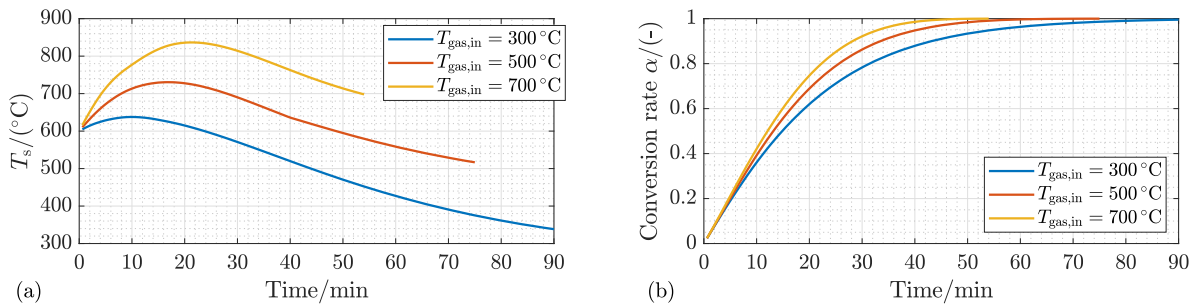


Figure 13. (a) Temporal trend of the solid phase temperature and (b) the related conversion rates at the different input gas temperatures of 300 °C, 500 °C and 700 °C during the oxidation process.

Figure 14 presents the estimated heat flow rates during the oxidation reaction. Similar to the reduction, the heat loss rates to the ambient air are mainly dependent on the temperature difference between the reactor wall temperature and the environment air. As shown in Figure 14(a), the trend of the heat transfer rates received by the ambient air are almost identical to the solid material temperature (see Figure 13(a)) and starts with nearly 0.06 kJ/s. The peak values reach a magnitude of nearly 0.115 kJ/s at an input gas temperature of 700 °C after 22 min of the reaction start. Considering the input gas temperature of 500 °C, the peak ambient heat rate of 0.09 kJ/s is obtained after 17 min.

According to a less distinctive temperature dependency of the oxidation conversion rate,

the heat of reaction, depicted in Figure 14(b), shows for all three considered cases a similar trend. The respective initial value is 0.53 kJ/s and the trend is falling, until a complete conversion of the solid material is reached. In terms of an gas input temperature of 700 °C the rising solid temperature accelerates the reaction kinetics and, consequently, the respective heat of reaction to a peak value of 0.55 kJ/s in the first 5 min. Between 24 and 26 min there is an intersection of the three graphs. This is mainly attributed to the fact that the integral heats of reactions amount to 781.4 ± 10 kJ, in the tested range of temperatures, which can be assumed constant. This implies that the increased heat rates at the higher temperatures at the beginning of the respective reaction shall be associated with a decreased heat rate after a certain reaction time.

The transferred heat flow between the gas and solid phases is displayed in Figure 14(c). It can be observed that, the gas phase is heated up by the solid phase and this heat rate diminishes after reaching a peak value as the temperatures of both phases tend to equalize with time. The respective peak heat rates between the gas and solid phases reach $\dot{Q}_{\text{gas}}(12 \text{ min}) = -0.34 \text{ kJ/s}$, $\dot{Q}_{\text{gas}}(18 \text{ min}) = -0.26 \text{ kJ/s}$ and $\dot{Q}_{\text{gas}}(22 \text{ min}) = -0.18 \text{ kJ/s}$ at 300 °C, 500 °C and 700 °C, respectively.

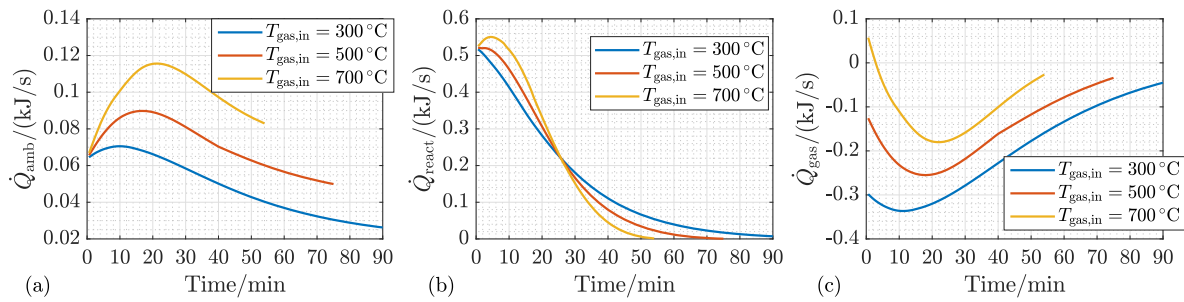


Figure 14. Temporal trends of the heat flow rates associated with the non-isothermal oxidation reaction at the different input gas temperatures of 300 °C, 500 °C and 700 °C; (a) Heat transfer rate received by the ambient air $\dot{Q}_{\text{amb}}$; (b) Heat rate of reaction $\dot{Q}_{\text{react}}$; (c) Exchanged heat between the gas and solid phases $\dot{Q}_{\text{gas}}$.

3.5. Serial connection of five non-isothermal reactors

In this sub-section the results of connecting five of the previously investigated non-isothermal reactor are connected in series and simulated to elaborate the influence of the variable input gas temperature and concentration on the temporal reactive performance of the included storage mass in each reactor. Table 7 defines the initial values of the state variables as well as the operating condition, under which the explained serial connection is investigated. The results presented afterwards include the temporal solid phase temperature and its conversion rate inside each reactor as well as the hydrogen and water vapor concentrations at the exit of each reactor, which represent the inlet concentrations into the next successive reactor. The investigations encounter both a reduction process and an oxidation process for the defined operating conditions in Table 7.

The results for the reduction phase with a gas temperature of 700 °C entering the very first reactor (R1) are presented in Figures 15 and 16. Figure 15(a) illustrates the temporal solid material temperatures inside each reactor (R1 to R5). Here, the solid material inside the first reactor attains the exact temperature evolution in the single reactor investigated in the last sub-section. The gas stream leaving the first reactor (R1), and entering R2, shall have almost the same temporal temperature trend. Accordingly, the reaction temperature and, consequently, the conversion rate become slower and slower upon moving from R2 until R5.

It can be observed that, the temperature of the last reactor (R5) decreases to $T_s = 524$ °C at 60 min and shows an end temperature of about $T_s = 585$ °C. The related conversion rates $\alpha(t)$

Table 7. Initial values of the state variables and the operational case conditions to be studied with the serial connection of five identical reactors.

Symbol	Description	Value		Unit
		Reduction	Oxidation	
$u(t=0)$	Oxidation fraction	1	0	-
$\dot{n}_{\text{gas,in}}$	Input mole flow (gas phase)	0.5	0.5	kmol/h
$T_{\text{gas,in}}$	Input temperature (gas phase)	700	500	°C
$x_{\text{H}_2,\text{in}}$	Input hydrogen mole fraction	0.8	-	-
$x_{\text{H}_2\text{O},\text{in}}$	Input steam mole fraction	-	0.8	-
$x_{\text{N}_2,\text{in}}$	Input nitrogen mole fraction	0.2	0.2	-
$m(t=0)$	Solid mass	5×2.0	5×1.51	kg
$T_s(t=0)$	Fixed bed temperature (solid phase)	800	600	°C

are depicted in Figure 15(b). Here, the conversion rate rises the fastest inside R1 and reaches a fully converted state after 160 min. The later on reactors start with a certain delay. For example, over the first six minutes, the solid phase inside R5 does not start the reduction reaction as the hydrogen mole fraction threshold at its input, which is estimated by the equilibrium constant out of equation (13), is not yet reached. It can be, furthermore, observed that R5 reaches only a conversion rate of $\alpha(t) = 0.965$ at the end of the considered time interval of 360 min.

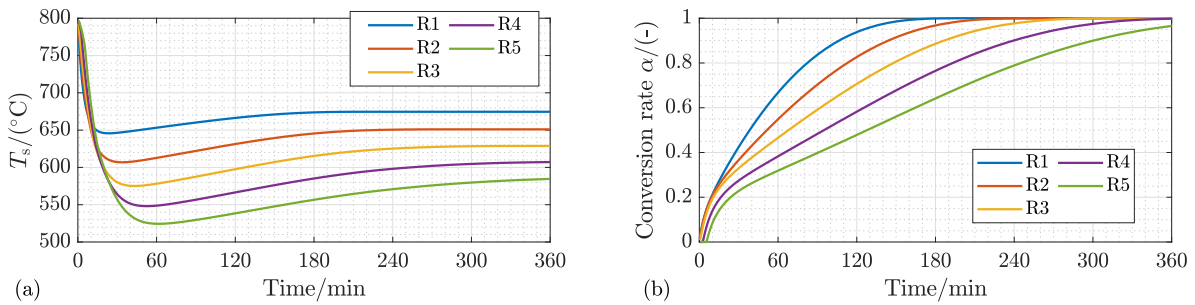
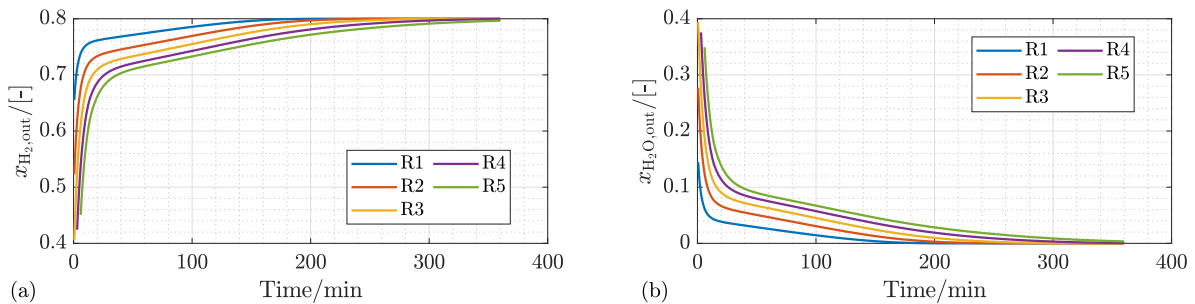
**Figure 15.** (a) Temporal solid material temperatures inside the five reactors R1 to R5 and (b) the related conversion rates at an input gas temperature of 700 °C for the reduction phase.

Figure 16(a) visualizes the temporal H_2 -concentration, while Figure 16(b) depicts the temporal H_2O -concentration of the exit streams of each reactor. The molar gas flow rate entering the first reactor (R1) is set to $\dot{n}_{\text{gas}} = 0.5 \text{ kmol/h}$ and the hydrogen mole fraction equals 80% as presented in Table 7. At the exit of R1, the mole fraction of hydrogen drops to a minimum of 66% before it rises again during the reduction phase until it reaches the inlet mole fraction after ca. 200 min. Because of the gas concentration and temperature dependence of the successive active masses in R2 to R5, their conversion rates and, accordingly, their exit gas concentrations drop further and are clearly slower than R1. As explained before, the hydrogen mole fraction threshold to start the reduction reaction, which is estimated based on equation (13) is reached for R3 after 3 min and for R5 after 6 min.

**Figure 16.** Temporal molar gas concentrations at the exit of each reactor R1 to R5 during the reduction phase at an input gas temperature of 700 °C; (a) Hydrogen H_2 ; (b) Steam H_2O .

The results for the oxidation phase are presented in Figures 17 and 18. Figure 17(a) displays the temporal temperature trend of the solid material inside each reactor. Due to the lowest input gas stream temperature of 500 °C into the first reactor, its solid phase cooled down over the entire oxidation process. Because of the exothermic nature of the oxidation process, the gas stream is continuously heated up in R1 to R5, so that the solid phase temperature inside R5 exhibits a peak value of almost $T_s = 742$ °C after 20 min, before it drops again and reaches 565 °C after 60 min.

The associated conversion rates $\alpha(t)$ of the oxidation reaction are presented in Figure 17(b). Based on our previous results [20], the temperature dependency of the oxidation kinetics is not as distinctive as the kinetics of the reduction phase. However, the negative influence of having a lower mole fraction of the reactive component entering each successive reactor is obviously counteracted by the elevated temperatures of the solid mass (Figure 17(a)), so that the conversion rates inside all reactors don't vary quite much, despite the trend to be a bit slower from R1 to R5 as depicted in Figure 17(b).

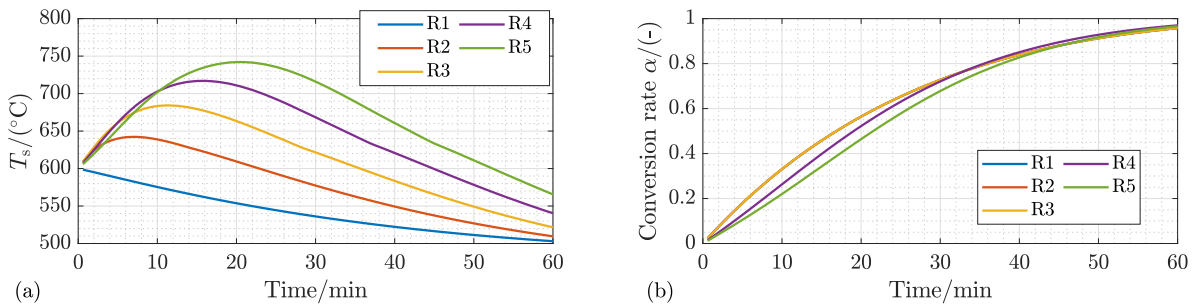


Figure 17. (a) Temporal trend of the solid material temperature inside the five reactors R1 to R5 and (b) the related conversion rates at an input gas temperature of 500 °C for the oxidation process.

The mole fractions of the output gas streams from each reactor during the oxidation phase are presented in Figure 18(a) with the respective H_2 -mole fractions and in Figure 18(b) for the H_2O -mole fractions. The input mole fraction of H_2O into R1 amounts to 80% as defined in Table 7. This steam mole fraction drops first in R1 down to H_2O -fraction of 67% at the beginning of the oxidation process and recovers approaching the inlet mole fraction, as the reaction time proceeds. The respective temporal steam mole fractions of the outlet streams from R2 to R5 follow R1, however with a clear time lag. As stated before, this trend, if alone, should have a negative influence on the conversion rates of the later reactors, which is indeed compensated by the enhanced solid phase temperatures resulting in a slight slow down of the conversion rates between R1 and R5 as can be seen in Figure 17(b).

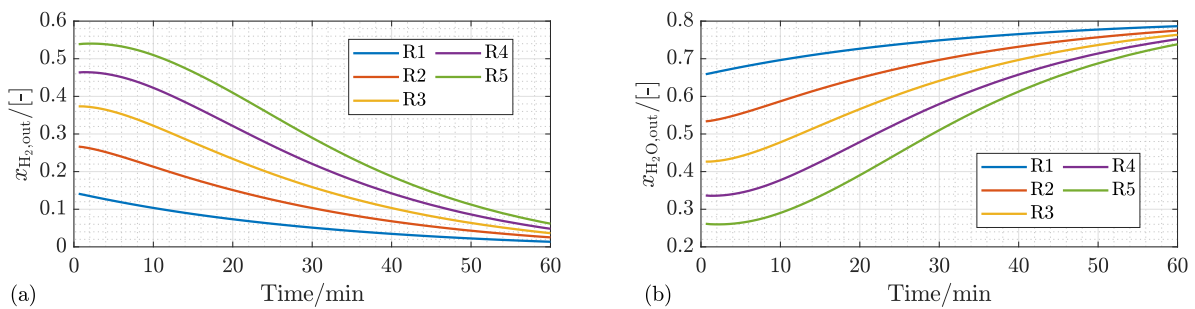


Figure 18. Temporal trends of the molar fractions of hydrogen and steam of the exit streams of R1 to R5 during the oxidation phase at an input gas temperature of 500 °C; (a) Hydrogen H_2 ; (b) Steam H_2O .

4. Conclusion

In this work, a dynamic lumped model for the isothermal reduction and oxidation (redox) reactions of a single iron oxide / iron pellet inside a gas stream of different hydrogen/steam concentrations, respectively, has been developed. To validate the model, the simulation results have been compared with the obtained experimental data under different isothermal conditions and concentrations of the respective reacting gas. Beside the temporal sample mass, the simulation model is applied to evaluate the temporal molar concentrations of the gas streams, the temporal molar quantities within the solid phase and reaction heat rates. An isothermal storage process comprising a charging (reduction) and a discharging (oxidation) phases, with a storage (holding) phase in between for a single pellet has been experimentally measured and simulated. The main outcomes of the isothermal model investigations can be summarized as follows:

- Both measured concentration- and temperature-dependent oxidation and reduction rates can be reproduced with the introduced isothermal model with a maximum deviation of 4.6% for the oxidation and 3.1% for the reduction reactions.
- The reaction temperature has a higher influence on the reduction reaction kinetics than on the oxidation reaction kinetics, which is attributed to the almost four times higher magnitude of the activation energy for reduction $E_{a,R} = 56.9 \text{ kJ/mol}$ compared to $E_{a,O} = 16.0 \text{ kJ/mol}$ for oxidation.
- Increasing the hydrogen concentration in the input gas stream from $x_{\text{H}_2,\text{in}} = 50\%$ to $x_{\text{H}_2,\text{in}} = 80\%$ at the reduction reaction temperature of 700°C results in enhancing the mass specific peak heat flow rate from $\dot{q}_{R,\text{ro}_2} = 110 \text{ W/kg}$ to $\dot{q}_{R,\text{ro}_3} = 156 \text{ W/kg}$.
- The same steam concentration change from $x_{\text{H}_2\text{O},\text{in}} = 50\%$ to $x_{\text{H}_2\text{O},\text{in}} = 80\%$ is associated with enhancing the mass specific peak heat flow rate from $|\dot{q}_{O,\text{ro}_2}| = 219 \text{ W/kg}$ to $|\dot{q}_{O,\text{ro}_3}| = 311 \text{ W/kg}$ during the oxidation reaction.
- For the considered isothermal and reversible redox reactions, the amount of heat converted or the time integral of the temporal heat flow rate is constant for both reduction and oxidation reactions with a slight dependency on temperature. The obtained heat of reactions amount to 404 kJ/kg at 600°C , which is varied to 395 kJ/kg at 800°C .

In addition, a non-isothermal lumped model has been developed for a tubular pelletized reactor containing 2 kg of iron oxide pellets. The non-isothermal model has been utilized to study the dynamics of both reduction and oxidation phases under different operating conditions as well as to explore the influence of connecting several reactors in series on the reactive performance of each storage mass under the varying input gas temperatures and mole fractions. The main outcomes of the non-isothermal model investigations can be summarized as follows:

- For the reduction process, elevated input gas temperatures are required to maintain the solid phase temperature above 400°C . According to the high temperature dependency of the reduction reaction, lower temperatures imply low reaction rates up to a complete stop of the reaction.
- Due to the less distinctive temperature dependency of the oxidation process, the input gas temperature has a lower impact on the conversion rate. However, lower gas temperatures of 300°C to 500°C are needed to cool down the reactive solid material, thus limiting the overheating due to the exothermic reaction and the associated material damage.
- Investigating the series connection of five reactors showed that, the reduction operation phase needs more control effort, especially if a reduced reduction duration is targeted. In comparison, the oxidation phase needs a special care to keep the temperature of the solid phase below the sintering temperature (800°C) to avoid the related dramatic slow down of the process.

The obtained results pave the way towards the establishment of a discretized non-isothermal storage model for in-depth investigation and validation of our coming experimental

investigations on the realized tubular pelletized reactor and applying the obtained results in the further development tasks of the hydrogen storage system.

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Conflicts of Interests

The authors declare no conflict of interest.

Authors' Contribution

Conceptualisation, B.G. and B.D.; Methodology, B.G. and S.E.; Software, B.G. and S.E.; Validation, B.G.; Formal analysis, B.G., S.E. and B.D.; Investigation, B.G. and S.E.; Resources, B.G. and B.D.; Data curation, B.G. and S.E.; Writing—original draft preparation, B.G. and S.E.; Writing—review and editing, B.G., S.E. M.G. and B.D.; Visualisation, B.G. and S.E.; Supervision, M.G. and B.D. All authors have read and agreed to the published version of the manuscript.

Nomenclature

Symbol	Description	Unit
A	Pre-exponential factor	1/s
A_{trans}	Internal heat transfer area	m ²
a, b	Constants in the equilibrium constant correlation	-
C	Molar gas fraction	-
$c_{\text{mol,gas}}$	Molar gas concentration	kmol/m ³
$c_{\text{p,mass,st}}$	Specific heat capacity of stabilizer mass	kJ/(kg·K)
$c_{\text{p,mol,gas}}$	Molar heat capacity of gas stream	kJ/(kmol·K)
$c_{\text{p,mol,Fe}}$	Molar heat capacity of iron	kJ/(kmol·K)
$c_{\text{p,mol,Fe}_3\text{O}_4}$	Molar heat capacity of magnetite	kJ/(kmol·K)
D	Internal reactor diameter	m
d_p	Pellet diameter	m
E_a	Activation energy	kJ/kmol
H	Reactor height	m
h_{amb}	External heat transfer to ambient	W/(m ² ·K)
$h_{\text{mol,gas}}$	Molar enthalpy of gas stream	kJ/kmol
$h_{\text{mol,Fe}_3\text{O}_4}$	Molar enthalpy of magnetite	kJ/kmol
$h_{\text{mol,Fe}}$	Molar enthalpy of iron	kJ/kmol
h_{trans}	Internal heat transfer coefficient	W/(m ² ·K)
K_{eq}	Equilibrium constant	-
k_A	Reaction velocity rate	1/s
k_{gas}	Thermal conductivity of gas	W/(m·K)
k_{iso}	Thermal conductivity of insulation	W/(m·K)
$M_{\text{Fe}_3\text{O}_4}$	Molar mass of magnetite	kg/kmol
M_{O_2}	Molar mass of oxygen	kg/kmol
m_0	Initial sample mass	kg

Symbol	Description	Unit
m_R	Initial active reaction mass	kg
m_{st}	Mass of stabilizing material	kg
$m(t)$	Mass of iron oxide/iron	kg
m_∞	Infinite sample mass	kg
Nu	Nusselt number	-
n	Empirical exponent	-
$n_{Fe}(t)$	Molar quantity of iron	kmol
$n_{Fe_3O_4}(t)$	Molar quantity of magnetite	kmol
$\dot{n}_{gas}$	Molar gas flow	kmol/s
p	Reactor pressure	bar
Pr	Prandtl number	-
$\dot{Q}_{amb}$	Ambient heat flow	kJ/s
$\dot{Q}_{gas}$	Gas-solid phase exchanged heat flow	kJ/s
$\dot{Q}_{react}$	Reaction heat flow	kJ/s
$r_{p,0}$	Initial pellet radius	m
$r_k(t)$	Reaction layer radius within the pellet	m
R	Gas constant	kJ/(kmol·K)
Re	Reynold number	-
T	Absolute temperature	K
T_{amb}	Ambient temperature	°C
$T_{gas,in}$	Gas inlet temperature	°C
$T_{gas,out}$	Gas outlet temperature	°C
T_s	Solid phase temperature	°C
T_w	Reactor wall temperature	°C
t	Time	s
$u(t)$	Oxidation fraction	-
u_0	Flow velocity of gas stream	m/s
$x_{H_2,in}$	Gas inlet molar fraction of hydrogen	-
$x_{H_2O,in}$	Gas inlet molar fraction of steam	-
x_{st}	Stabilizer mass fraction	-
$\alpha(t)$	Conversion rate	-
$\Delta\dot{n}_{H_2}$	Converted molar flow of hydrogen	kmol/s
$\Delta\dot{n}_{H_2O}$	Converted molar flow of steam	kmol/s
δ_{iso}	Thermal insulation thickness	m
ε_{bed}	Bulk porosity	-
ρ_{gas}	Gas density	kg/m ³
ρ_p	Single pellet density	kg/m ³
ρ_s	Solid bulk density	kg/m ³
η_{gas}	Dynamic viscosity of gas	Pa·s

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