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# A generic solar-thermochemical reactor model with internal heat diffusion for counter-flow solid heat exchange

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ABSTRACT

For nonstoichiometric redox reactions that produce CO and $H_2$ from $CO_2$ and $H_2O$, heat recuperation from the solid phase is a promising mechanism to improve the cycle efficiency. Many different approaches to heat recuperation and gas separation have been presented in solar thermochemical reactor concepts recently. To describe the many possible degrees of freedom in the reactor design, a generic reactor model is described for two-step redox reactions of solid pieces of reactant moving in counter flow between reduction and oxidation chambers. The reactive material is assumed to be porous ceria, where heat recuperation from the solid phase is achieved through radiation heat exchange between reduced and oxidized elements moving in opposite directions. A separation wall prevents gas cross-over and provides structural support. Heat transfer by radiation in the porous material is modeled with the Rosseland diffusion approximation and by conduction with the three resistor model. The model can be adapted to a wide range of reactor concepts.

A study of crucial design parameters shows that heat diffusion in the reactive material can have a significant influence on the performance of the heat exchanger. If the time required for heat diffusion is large with respect to the total residence time in the heat exchanger, the material thickness can be decreased to enhance the share of the material actively participating in the heat exchange process. Furthermore, at the relevant temperatures, radiation dominates the heat exchange within the porous structure, thus the overall heat exchange can be enhanced through an increase of porosity. Heat exchanger length and residence time are correlated, allowing different combinations of these two variables at constant heat exchanger efficiency. In general, efficiencies close to 70% are possible with an adequate parameter combination. However, the achievement of the maximum heat exchanger efficiency requires a minimum number of chambers and thus physical length, as irreversibilities are reduced for a larger number of intermediate temperature levels.

The presented generic model includes the description of heat diffusion within the reactive material, is a valuable tool for the design of heat exchangers, and can be used to identify technically interesting reactor concepts for the achievement of high energy conversion efficiencies.



## 1. Introduction

The transition of the energy basis from conventional sources such as coal, natural gas, and crude oil, to renewable sources is a major challenge that involves large investments and the development of new energy technologies. In case of the generation of electrical energy, a significant increase in renewable generation capacity has been achieved in the past years reaching a share of 22% of the total electricity generation (International Energy Agency, 2016). In the transportation sector, however, the penetration with renewables has been considerably lower, owing to the fact that conventional fuels such as gasoline, diesel and jet fuel are ideally suited for the use in mobile applications. Their high energy and power density are requirements for the use in aviation, sea traffic and heavy-duty road transportation, while for light-duty road transportation, an electrification using batteries and electric motors is easier to implement and has seen a rising share in recent years. Given a rising demand at limited resources and concerns about climate change, the aim of a reliable and affordable energy source for transportation requires solutions such as the production of an energy-dense fuel based on renewable energy.

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**Nomenclature**

| | |
|---|---|
| $A$ | area [$m^2$] |
| $A_{he,ext}$ | external area of heat exchanger chamber facing the environment [$m^2$] |
| $C$ | concentration ratio of solar radiation [–] |
| $c_{p,CeO_2}$ | heat capacity of ceria at constant pressure [J $mol^{-1}$ $K^{-1}$] |
| $c_{p,CO}$ | heat capacity of CO at constant pressure [J $mol^{-1}$ $K^{-1}$] |
| $c_{p,CO_2}$ | heat capacity of $CO_2$ at constant pressure [J $mol^{-1}$ $K^{-1}$] |
| $c_{p,O_2}$ | heat capacity of $O_2$ at constant pressure [J $mol^{-1}$ $K^{-1}$] |
| $d_{mean}$ | mean diameter [m] |
| $g_0$ | parameter used in the three resistor model [–] |
| $g_1$ | parameter used in the three resistor model [–] |
| $\Delta H_{red}$ | reduction enthalpy [J $mol^{-1}$] |
| $I$ | intensity of solar radiation [W $m^{-2}$] |
| $k_f$ | thermal conductivity of fluid phase [W $m^{-1}$ $K^{-1}$] |
| $k_s$ | thermal conductivity of solid phase [W $m^{-1}$ $K^{-1}$] |
| $m$ | number of computational layers in element of reactive material [–] |
| $N$ | number of calculations [–] |
| $\dot{n}_{CeO_2}$ | molar flow rate of ceria [mol $s^{-1}$] |
| $\dot{n}_{CO}$ | molar flow rate of CO [mol $s^{-1}$] |
| $\dot{n}_{CO_2}$ | molar flow rate of $CO_2$ [mol $s^{-1}$] |
| $\dot{n}_{O_2}$ | molar flow rate of oxygen [mol $s^{-1}$] |
| $p_{O_2}$ | oxygen partial pressure relative to standard state [–] |
| $P_{aux}$ | auxiliary electrical power needed to operate reactor [W] |
| $P_{pump}$ | electrical power required for operation of vacuum pump [W] |
| $P_{sep,CO/CO_2}$ | electrical power required for gas separation of $CO/CO_2$-mixture [W] |
| $\dot{Q}_{aux}$ | solar power needed for auxiliary processes [W] |
| $\dot{Q}_{heat,CeO_2}$ | solar power needed to heat ceria [W] |
| $\dot{Q}_{heat,CO_2}$ | solar power needed to heat $CO_2$ [W] |
| $\dot{Q}_{heatexchange}$ | net rate of energy transferred between ceria elements in upper chamber half and lower chamber half of heat exchanger [W] |
| $\dot{Q}_{loss,conv}$ | thermal power lost by convection from heat exchanger chamber half [W] |
| $\dot{Q}_{loss,rad}$ | thermal power lost by radiation from heat exchanger chamber half [W] |
| $\dot{Q}_{products}$ | thermal power recovered from gaseous products [W] |
| $\dot{q}_{rad}$ | radiative heat flux [W $m^{-2}$] |
| $\dot{Q}_{red,CeO_2}$ | solar power needed to reduce ceria [W] |
| $\dot{Q}_{rerad}$ | rate of radiation heat losses from the reduction chamber [W] |
| $\dot{Q}_{solar}$ | solar power input to reactor [W] |
| $\mathscr{R}$ | ideal gas constant [J $mol^{-1}$ $K^{-1}$] |
| $s$ | sample standard deviation [–] |
| $\Delta t$ | residence time in heat exchanger chamber [s] |
| $t_{CI,v}$ | t-value of the student t function for the confidence interval CI and $v = N - 1$ degrees of freedom |
| $T$ | temperature [K] |
| $T_0$ | ambient temperature [K] |
| $T_H$ | reduction temperature [K] |
| $T_{he,end,j}$ | temperature of $j$-th layer of reactive material at the end of the heat exchanger [K] |
| $\overline{T}_i$ | arithmetic mean temperature at position i |
| $T_L$ | oxidation temperature [K] |
| $T^n$ | temperature in time step $n$ [K] |
| $T^{n+1}$ | temperature in time step $n+1$ [K] |
| $T_{pump}$ | temperature of vacuum pump [K] |
| $T_{RPC\rightarrow sw}$ | temperature of RPC in lower chamber half facing separating wall [K] |
| $T_{sw\rightarrow RPC}$ | temperature of separating wall facing RPC in lower chamber half [K] |
| $T_{wall}$ | temperature of heat exchanger wall facing surroundings [K] |

*Greek letters*

| | |
|---|---|
| $\alpha$ | absorption coefficient in Monte Carlo analysis [–] |
| $\alpha_{conv}$ | convective heat transfer coefficient at heat exchanger wall [W $m^{-1}$ $K^{-1}$] |
| $\beta$ | extinction coefficient [$m^{-1}$] |
| $\beta_R$ | Rosseland mean attenuation coefficient [$m^{-1}$] |
| $\delta$ | oxygen nonstoichiometry of ceria [–] |
| $\delta_{ox}$ | oxygen nonstoichiometry of oxidized ceria [–] |
| $\delta_{red}$ | oxygen nonstoichiometry of reduced ceria [–] |
| $\varepsilon_{CeO_2}$ | emissivity of ceria [–] |
| $\varepsilon_{sw}$ | emissivity of separating wall [–] |
| $\varepsilon_{wall}$ | emissivity of heat exchanger wall facing the environment [–] |
| $\eta$ | efficiency (concentrated solar to chemical energy stored in CO) [–] |
| $\eta_{abs}$ | absorption efficiency of reactor [–] |
| $\eta_{gasrec}$ | recuperation efficiency of gases leaving the reduction and oxidation chambers [–] |
| $\eta_{he}$ | heat exchanger efficiency [–] |
| $\eta_{heat-to-electricity}$ | conversion efficiency of heat to electricity [–] |
| $\eta_{pump}$ | efficiency of vacuum pump [–] |
| $\lambda$ | thermal conductivity [W $m^{-1}$ $K^{-1}$] |
| $\lambda_{rad}$ | radiative conductivity [W $m^{-1}$ $K^{-1}$] |
| $\sigma$ | Stefan-Boltzmann constant [W $m^{-2}$ $K^{-4}$] |
| $\varphi$ | porosity [–] |
| $\Psi_1$ | parameter used in the calculation of the extinction coefficient [–] |

Due to its abundance and global availability, solar energy is an attractive primary energy source for the production of liquid fuels. The solar thermochemical pathway uses concentrated solar energy to thermochemically split water and carbon dioxide into syngas and the Fischer-Tropsch process to synthesize liquid hydrocarbon fuels. It offers the potential of a low climate impact at a large energy conversion efficiency (Falter et al., 2016; Steinfeld and Epstein, 2001). For its implementation, different materials and processes have been suggested, where in recent years, non-volatile redox reactions with cerium oxide (ceria) have shown promising experimental results (Chueh et al., 2010; Furler et al., 2014, 2012a; Marxer et al., 2015). In most implementations, ceria is only partially reduced to retain the material in its solid fluorite structure and to thus enable a process without phase changes. This facilitates the reactor design considerably, as high temperature gas separations are avoided. However, the downside is that only a small fraction of the reactive material actually participates in the redox cycle, leading to a large thermal mass with respect to the produced amount of syngas. As the redox cycle is performed under a temperature swing, a relatively large amount of energy is required for the heating of the material to the reduction temperature. In theoretical analyses it was shown that for nonstoichiometric ceria cycles, energy recuperation from the temperature swing is imperative to achieve high levels of energy conversion efficiency (Falter et al., 2015; Lapp et al., 2012).

Different reactor concepts have been presented including heat recuperation from the solid and the gaseous phase, e.g. the CR5-reactor (Diver et al., 2008), where counter-rotating rings of reactive material are reduced by solar radiation on one side and oxidized on the opposite side, exchanging heat in between the reaction zones. Another similar concept is shown in Lapp et al. (2013), where an inert cylinder rotates in the opposite direction of the reactive