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Transient heat transfer simulation of a 1 kWth moving front solar thermochemical reactor for thermal dissociation of compressed ZnO

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ABSTRACT

A 1 kWth cavity-type solar reactor devoted to the thermal reduction of volatile oxides as part of a two-step thermochemical cycle is analyzed numerically. The thermochemical reactor consists of a vertical-axis cavity-type receiver in which the reactant is injected from the bottom in the form of an ascending rod made of a stack of zinc oxide compressed pellets undergoing thermal dissociation. A transient heat transfer model allows the simulation of the thermal behavior under real conditions for the rod of reacting particles exposed to concentrated solar radiation. The developed numerical model couples radiation, conduction and convection heat transfers to the kinetic of the reaction. The incident solar irradiation on the reactant surface is obtained using the Monte-Carlo ray tracing technique applied first to the solar concentrator and second to the reactor cavity. The model is used to predict the temperature profile from the irradiated front surface of the compressed reactant, the evolution of outlet oxygen molar flow-rate during the reduction reaction and the instantaneous thermochemical efficiency, as a function of time. The calculated results are compared with the experimentally obtained data. The agreement between experimental data and simulation related to both the temperature and the oxygen progress is fairly good with $E_a = 380\,\mathrm{kJ\,mol^{-1}}$ and $k_0 = 246 \times 10^6\,\mathrm{mol\,m^{-2}\,s^{-1}}$ for the kinetics of the ZnO dissociation reaction.

Keywords: Solar hydrogen production; Zinc oxide reduction; Solar fuels; Solar reactor simulation; Monte Carlo method; Solar energy storage

1. Introduction

The use of concentrated solar radiation as the energy source in high-temperature thermochemical processes is a promising alternative to carry out materials transformation while reducing the emission of greenhouse gases. Some examples are: the calcination of calcium carbonate for solar production of lime or cement (Meier et al., 2005), the detoxification and recycling of hazardous wastes (Funken et al., 1999), the production of energy carriers, such as hydrogen or synthesis gas (Kodama, 2003), among others.

In particular, the production of clean "solar hydrogen" is a preponderant sustainable application that is focused on the future substitution of fossilfuels, and the reduction of

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Nomenclature

a	specific surface area (m^{-1})
A	rod surface area (m^2)
c_p	specific heat capacity ($J\,kg^{-1}\,K^{-1}$)
E_a	activation energy ($kJ\,mol^{-1}$)
F_{p-c}	view factor
F_{O_2}	oxygen molar flow rate ($mol\,s^{-1}$)
$f_{0,\lambda}$	spectral irradiance distribution of the sun
G_s	incident solar irradiation ($W\,m^{-2}$)
h	heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
ΔH	enthalpy change (J/mol)
k	thermal conductivity ($W\,m^{-1}\,K^{-1}$)
k_0	pre-exponential factor ($mol\,m^{-2}\,s^{-1}$)
M	molar mass ($kg\,mol^{-1}$)
m	mass (kg)
n	refraction index
P_{solar}	solar power input (W)
Q	volumetric heat sink ($W\,m^{-3}$)
q''	heat flux density ($W\,m^{-2}$)
r'''	reaction rate ($mol\,m^{-3}\,s^{-1}$)
R	reflectance
R_g	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
T	rod surface temperature (K)
t	time (s)
T_b	rod bottom temperature (K)
T_{cavity}	cavity temperature (K)
T_g	inert gas temperature (K)
V	volume (m^3)
z_L	rod length (m)

Greek symbols

α_s	solar absorption coefficient
β	extinction coefficient (m^{-1})
ε	emissivity
φ	ratio of reactant surface area to exposed ZnO volume (m^{-1})
ρ	density ($kg\,m^{-3}$)
η	thermochemical efficiency
σ	Stefan–Boltzmann constant ($W\,m^{-2}\,K^{-4}$)
λ	wavelength (m)

Subscripts

b	bottom
chem	chemical
cond	conduction
eff	effective
f	front
l	lateral
0	initial
rad	radiation
s	solar

Dimensionless group

Ra	Rayleigh number
Nu	Nusselt number
Pr	Prandtl number

greenhouse gas emissions. An attractive and promising route to obtain this energy carrier relies on the two-step thermochemical water-splitting cycles. These processes are attractive with respect to electrolytic or photolytic routes, mainly because they present satisfactory energy efficiency due to the direct conversion of heat to hydrogen (Abanades et al., 2006). This method has the advantage of producing long-term storable and transportable energy carriers from solar energy.

Previous studies have shown that the two-step cycle based on the ZnO/Zn redox pair is a well suited process for the "solar hydrogen" production due to high energy conversion efficiencies reached, relatively moderate reaction temperatures (below 2200 K), and rapid kinetics in the hydrolysis reaction (Bilgen and Bilgen, 1981; Steinfeld, 2002; Vishnevetsky and Eptein, 2007). This cycle comprises the solar thermal dissociation of ZnO(s) at high temperatures, which produces gaseous volatile Zn species and O_2, followed by the non solar exothermic reaction of the Zn recovered as condensed solid particles with H_2O, which generates H_2 and the initial oxide that can be recycled to the first step:

$$ZnO \rightarrow Zn + 0.5O_2 \quad \text{Solarendothermicstep} \tag{1}$$

$$Zn + H_2O \rightarrow ZnO + H_2 \quad \text{Non-solarendothermicstep} \tag{2}$$

The endothermic step of this cycle is the most critical issue of the process. A challenge of solar thermochemical engineering is the optimization of solar reactors design. Therefore, the design and operation of novel receiver/reactor systems capable of efficiently collecting concentrated solar radiation and performing high-temperature reactions is the main objective in this field. Recently, this cycle was implemented at CNRS-PROMES laboratory by using 1 kWth solar reactor prototypes designed for the continuous thermal reduction of volatile metal oxides (Chambon et al., 2010, 2011). A promising reactor concept features a static vertical-axis cavity-type receiver with a metal oxide rod that is pushed forward by a screw piston. With this reactor configuration, the reactant front surface is directly irradiated with concentrated solar energy. Solar reactors based on this configuration allow reaching higher thermal efficiencies due to the more efficient energy transfer to the reaction site, thereby eliminating the limitations associated to an indirect heating, namely the induced additional heat losses along with the restrictions imposed by the selection of materials of the heat transfer medium that must be resistant to high temperatures.

In order to optimize or scale-up solar reactors, parameters such as the reactor volume, maximum working temperature, physicochemical properties of construction materials and reactants, and temperature distribution have to be optimized, taking into account the heat transfer characteristics, the reaction rates and the transient phenomena due to the random nature of the solar flux irradiation.

Several studies have dealt with solar reactor modeling (Valdes-Parada et al., 2011; Villafán-Vidales et al., 2009, 2011; Abanades et al., 2007; Martinek et al., 2012; Kraüpl and Steinfeld, 2005), but only a few have analyzed the transient behavior of these systems (Dombrovsky et al., 2009; Schunk et al., 2009a,b). The present work is focused on the development of a transient heat transfer model accounting for chemical reaction for a lab-scale cavity-type solar reactor devoted to the thermal reduction of ZnO, as part of a two-step thermochemical cycle (Chambon et al., 2011). The developed transient model couples radiation, conduction, and convection heat transfer modes with the reaction rate. The model is used to determine the thermal behavior of the solar reactor under representative conditions encountered during the experiments.