Transient simulation of a tubular packed bed solar receiver for hydrogen generation via metal oxide thermochemical cycles

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Abstract

Theoretical performance of a 4 kW multiple tube solar receiver is evaluated for a two-step thermochemical redox cycle using a transient computational fluid dynamics model coupling radiative transfer with fluid flow, heat transfer, mass transfer and chemical reaction kinetics. The solar receiver consists of an array of tubular absorbers, each containing a packed bed of active material and situated within an insulated outer cavity with a small aperture. Tubular array configurations amenable to either temperature swing or isothermal operation are included, though calculations predict temperature separation of at most 150–200 K between reduction and oxidation tubes positioned within a single well-insulated reaction vessel. Sensitivity of receiver performance to parameters describing material properties, operating conditions, cycle time, solar profile shape, tube dimensions, and tubular array configuration is assessed. Simulations indicate that receiver performance is most sensitive to aperture size with emission losses accounting for more than 50% of the solar input. An array consisting of a large number of small-diameter tubes is preferred, though performance is minimally impacted by the physical positions of these tubes within the receiver cavity. Time-averaged solar-to-chemical efficiency as high as 14% is predicted after accounting for energy necessary for O_2 separation and steam vaporization.

1. Introduction

The conversion of thermal energy derived from concentrated sunlight to chemical energy carriers such as hydrogen via thermochemical water splitting offers a pathway to sustainable fuels and long-term energy solutions. Direct thermolysis of water is theoretically possible but infeasible in practice as temperatures exceeding 2200 °C are required, thereby necessitating high solar concentration ratios, exotic materials for receiver construction, and effective high-temperature gas separation techniques for simulta-

neously generated hydrogen and oxygen (Fletcher and Moen, 1977; Nakamura, 1977). Metal oxide redox cycles are a promising alternative to direct thermolysis as they proceed at lower temperatures and bypass the necessity of high temperature gas separations via the generation of hydrogen and oxygen in discrete steps (Kodama and Gokon, 2007; Steinfeld, 2005). Traditional metal oxide water-splitting cycles proceed through a sequence of two steps: a highly endothermic oxygen-evolving reduction followed by a mildly exothermic re-oxidation of the reduced metal oxide with water to produce hydrogen. Traditionally, the process is carried out with $T_{red} > T_{ox}$ and candidate materials including CeO_2 (Abanades and Flamant, 2006; Chueh et al., 2010; Bader et al., 2013), ZnO (Palumbo
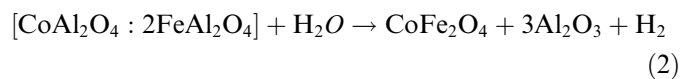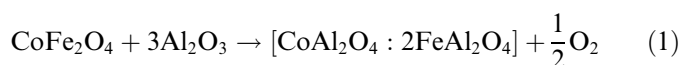
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Nomenclature

d_p	particle diameter (m)
d_{pore}	pore diameter (m)
C_p	heat capacity (J/kg/K)
$\hat{C}_p$	heat capacity (J/mol/K)
D	diffusivity (m^2/s)
e_{O2}	electricity required to separate O_2 from inert (J/mol)
E_i	activation energy for reaction i (J/mol)
F_{kj}	view factor between surfaces k and j
g	gravitational acceleration (m/s^2)
h	enthalpy (J/kg)
$I_{\lambda,b}$	spectral blackbody intensity
J	radiosity (W/m^2)
k	thermal conductivity (W/m/K)
$k_{0,i}$	reaction rate constant for reaction i
k_{rad}	radiative conductivity (W/m/K)
K	permeability (m^2)
K_{eq}	equilibrium constant
ℓ	window thickness (m)
LHV	lower heating value (J/mol)
M	molecular weight (kg/mol)
$\dot{n}$	molar flow rate (mol/s)
p	pressure (Pa)
Q_{solar}	solar power incident on receiver (W)
Q_{tot}	total thermal input (J)
R	reaction rate (mol/m^3/s)
R_r	quartz window reflectance
R_i	mass source of component i due to chemical reaction (kg/m^3/s)
$\vec{S}$	momentum "sink" due to packed bed (kg/m^2/s^2)
S_r	energy source due to reaction (W/m^3)
S_v	particle surface area per volume (m^{-1})
T	temperature (K)
T_r	quartz window transmittance
w	mass fraction
α	extent of reaction
β	extinction coefficient for packed bed (m^{-1})
ε	porosity
ε_r	surface emissivity

ε_{gas}	gas-phase heat recuperation effectiveness
$\bar{\eta}$	time-averaged solar-to-chemical receiver efficiency
$\eta_{s\text{-}e}$	solar-to-electric conversion efficiency
θ_c	width of cone describing incident solar energy
θ_a	aim angle for solar beam
κ	extinction coefficient
λ	wavelength (m)
μ	viscosity (kg/m/s)
ρ	density (kg/m^3)
ρ_r	surface reflectivity
$\bar{\rho}_r$	spectrally-averaged surface reflectivity
σ	Stefan–Boltzmann constant (W/m^2/K^4)
$\sigma_{x,y}$	standard deviation of Gaussian distribution describing solar flux profile
τ	transmissivity
$\bar{\tau}$	spectrally-averaged transmissivity
$\vec{\tau}$	viscous stress tensor (kg/m/s^2)
$\vec{v}$	velocity (m/s)
$\vec{v}_0$	superficial velocity (m/s)
ΔH	enthalpy of reaction (J/mol)
ΔH_{vap}	enthalpy of vaporization of steam (J/mol)

subscripts/superscripts

b	backward, blackbody
eff	effective
f	fluid, forward
in	inlet
p	particle
rad	radiative
red	reduction
ref	reference
s	solid
tot	total
out	outlet
ox	oxidation
λ	spectral

et al., 1998; Perkins et al., 2008), perovskites (McDaniel et al., 2013), and mixed metal ferrites of the form $M_xFe_{3-x}O_4$ where M typically represents Co, Ni, Mn, or Zn have been investigated extensively (Allendorf et al., 2008; Kodama et al., 2008, 2005; Miller et al., 2008; Scheffe et al., 2013). Ferrite materials exhibit theoretically greater H_2 yields than non-stoichiometric oxides and possess favorable thermodynamic properties including reduction temperatures on the order of 1400 °C. However, redox cycling commonly results in deactivation due to sintering or formation of liquid phases at temperatures only marginally above that required for reduction

(Allendorf et al., 2008; Gokon et al., 2008; Kodama et al., 2008). Scheffe et al. (2010) deposited a thin film of $CoFe_2O_4$ on an Al_2O_3 substrate and noted redox cycling occurring through an intermediate aluminate structure according to the following "hercynite" cycle reactions:

$$CoFe_2O_4 + 3Al_2O_3 \rightarrow [CoAl_2O_4 : 2FeAl_2O_4] + \frac{1}{2}O_2 \quad (1)$$

$$[CoAl_2O_4 : 2FeAl_2O_4] + H_2O \rightarrow CoFe_2O_4 + 3Al_2O_3 + H_2 \quad (2)$$