



A new solar fuels reactor concept based on a liquid metal heat transfer fluid: Reactor design and efficiency estimation

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Abstract

A new reactor concept for two-step partial redox cycles is presented and evaluated by transient simulation that considers heat and mass transfer along with reaction kinetics. The major difference between the reactor described herein and previous designs is that the conversion from solar to chemical energy is divided into two steps: sunlight-to-thermal energy conversion accomplished with a liquid metal based receiver, and the thermal-to-chemical conversion accomplished with a separately optimized array of reaction chambers. To connect these two conversion steps, liquid metal is used as a high temperature heat transfer fluid that feeds the solar energy captured in the receiver to the reactor. The liquid metal also facilitates efficient heat recuperation (~80%) between the reaction chambers. The overall thermal-to-chemical efficiency from the thermal energy in the liquid metal to the chemical energy in the hydrogen fuel is estimated to be 19.8% when ceria is employed as the reactive oxygen storage material. This estimated efficiency is an order of magnitude higher than previous designs and the reactor concept discussed herein identifies important insights that apply to solar–fuel conversion in general.

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1. Introduction

The idea of using solar energy as high temperature process heat to make fuel has been of interest for more than three decades (Funk and Reinstrom, 1966; Funk, 2001; Nakamura, 1977; Steinfeld, 2005; Steinfeld et al., 1995). This idea has gained increased attention over the last few years as attention has shifted to two-step partial redox cycles (Bader et al., 2013; Chueh and Haile, 2010, 2009; Chueh et al., 2010; Diver et al., 2008; Ermanoski et al., 2013; Furler et al., 2012; Keene et al., 2013; Lapp and

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Nomenclature

Abbreviations

HTF	heat transfer fluid
LM	liquid metal
LMHTF	liquid metal heat transfer fluid
OSM	oxygen storage material

Symbols

A_{rec}	surface area of the receiver
A_{reactor}	surface area associated with the reactor
$b_{\text{insulation}}$	thickness of insulation
C_p	heat capacity
d_{32}	OSM pore scale particle size
F	dimensionless energy factors
$h_{\text{insulation}}$	heat transfer coefficient of Insulation
H_{chamber}	height of chambers
HHV_{H_2}	higher heating value of H_2
L_{chamber}	length of chambers
\dot{m}_{OSM}	effective mass of the OSM
M_{OSM}	molar mass of the OSM
N_{pipe}	number of pipes inside of one chamber
n_{H_2}	total hydrogen production in a stage by a chamber
n_{O_2}	total oxygen production in a stage by a chamber
p_{O_2}	partial pressure of oxygen
p_{reactor}	reactor power
Q	heat input
\dot{q}	heat flux
R_{LM}	inner radius of pipe

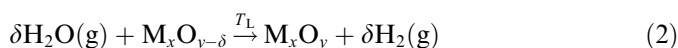
R_{Sup}	outer radius of pipe
R_{OSM}	outer radius including OMS
R_{fs}	radius of bulk gas layer
t_{pumping}	pumping time in reduction step
t_{purging}	purging time in reduction step
t_{preheat}	time to preheat the chambers
T	temperature profile
T_{H}	reduction step temperature
$T_{\text{H-}}$	initial chamber temperature of reduction step
T_{L}	oxidation step temperature
$T_{\text{L+}}$	initial chamber temperature of oxidation step
u_{LM}	velocity of LM
$u_{\text{gas,inlet}}$	inlet velocity of purging gas
W_{chamber}	width of chamber
Δt	cycle time
$\Delta\delta$	average change in off-stoichiometry
δ	nonstoichiometry
$\bar{\delta}_{\text{OSM}}$	average nonstoichiometry reached in OSM
ρ	density
λ	thermal conductivity
ε	porosity of OSM
ε_{S}	sensible heat recuperation efficiency
τ	tortuosity of OSM
η_{gas}	gas–gas heat exchanger efficiency
$\eta_{\text{thermal-chemical}}$	thermal to chemical efficiency
$\eta_{\text{solar-thermal}}$	solar to thermal efficiency
$\eta_{\text{solar-chemical}}$	solar to chemical efficiency

Lipiński, 2014; Lapp et al., 2012, 2013; Lipiński et al., 2013; Miller et al., 2012; Muhich et al., 2013; Siegel et al., 2013; Wei et al., 2013; Zinkevich et al., 2006) based on materials such as ceria, which have demonstrated hundreds of cycles with repeatable performance (Chueh et al., 2010). Two-step partial redox cycles using metal oxides undergo the following two reactions to make a fuel, such as hydrogen from water, which is the primary example discussed herein:

Step 1: Reduction Reaction



Step 2: Oxidation Reaction



In these reactions, the solid phase metal oxide serves as an oxygen storage material (OSM), signified by M_xO_y . The OSM is heated to a high temperature T_{H} (e.g. 1200–1500 °C) and is subjected to a low oxygen pressure (P_{O_2}) environment where it endothermically releases oxygen from its

lattice. The heat required to break the chemical bonds is supplied by the high temperature solar process heat and the oxygen release is driven by the entropy increase experienced by the O_2 molecules upon liberation. After step 1 the OSM is in a reduced state $\text{M}_x\text{O}_{y-\delta}$ and is then cooled to a lower temperature T_{L} (e.g. 500–800 °C), such that the thermodynamic driving force is reversed and the OSM consumes the oxygen in H_2O to refill its oxygen vacancies. This second reaction liberates hydrogen thereby producing fuel, while the OSM can be reheated and cycled through these two reaction steps without being consumed.

From a fundamental perspective, using sunlight as a source of thermal energy provides advantages over photocatalytic approaches, because the entire solar spectrum is utilized, as opposed to only using the high energy portion of the spectrum which is capable of splitting chemical bonds directly. Techno-economic analyses by Stechel et al. have shown that the thermochemical approach to solar fuels can be economically viable, if the solar to fuel efficiency of a system exceeds 20% (Kim et al., 2012, 2011; Siegel et al., 2013).

The overall efficiency of a solar thermochemical reactor is constrained by a steady state balance between the power

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