Critical limitations on the efficiency of two-step thermochemical cycles

Colby Jarrett [a], William Chueh [b], Cansheng Yuan [a,c], Yoshiaki Kawajiri [c],
Kenneth H. Sandhage [d,e], Asegun Henry [a,d,*]

[a] *George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, United States*
[b] *Department of Material Science and Engineering, Stanford University, United States*
[c] *School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, United States*
[d] *School of Materials Science and Engineering, Georgia Institute of Technology, United States*
[e] *School of Materials Engineering, Purdue University, United States*

Abstract

Previous models based on thermodynamic considerations have identified the properties desired for reactive oxides that can be used as oxygen storage materials in thermochemical cycles to produce fuel from sunlight. However, there are several important assumptions made in such models, such as the neglect of the energy required to preheat unreacted species and the assumption of constant vacuum pump efficiency. When these assumptions are relaxed, one comes to significantly different conclusions about the optimal reactor operating conditions. Furthermore, comparing two materials is not straightforward due to the high degree of coupling between material properties and reactor operating conditions. Herein, we describe a new framework for material comparison which employs a thermodynamic reactor model to predict the maximum possible efficiency of a given oxygen storage material. This model demonstrates how new materials can impact reactor performance and the limitations of such improvements.
© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Global warming, pollution, and diminishing reserves are all issues associated with energy derived from fossil fuels. These issues make the development of a clean, sustainable energy infrastructure an imminent, albeit difficult technological challenge (IEA, 2013; Chaisson, 2008; Aleklett et al., 2010; Ngoh and Njomo, 2012; Holladay et al., 2009). Although global energy consumption continues to grow, it is still several orders of magnitude less than the energy received by the earth through solar radiation (Chueh and Haile, 1923). Photovoltaics and concentrated solar thermal power are becoming more established technologies for grid electricity production, but the challenge of finding a path to a renewable and dispatchable fuel for the transportation sector remains a daunting challenge. One promising approach is to store the sun's energy chemically by splitting water to produce hydrogen, which would serve as a dispatchable fuel or fuel precursor. A version of this process, termed thermolysis, can be achieved through the direct splitting of water molecules:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{1}$$

---

* Corresponding author at: George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, United States.
  E-mail address: ase@gatech.edu (A. Henry).

Nomenclature

Abbreviations

OSM	oxygen storage material
NRC	nonstoichiometric redox cycle
P_{O_2}	oxygen partial pressure
W_{Pump}	work to drive vacuum pump
T_H	reduction temperature
T_L	oxidation temperature
Q_{Total}	total energy input to system
Q_{Reheat}	energy needed to heat from T_L to T_H
Q_{RXN}	energy of endothermic reduction reaction
Q_{Water}	energy needed to generate steam
Q_{Out}	energy removed when cooling from T_H to T_L
ε_S	efficiency of solid phase heat recovery
ε_G	efficiency of gas phase heat recovery
Δt	cycle time
$\dot{Q}_{Loss}$	heat leak rate from the system
$M_xO_{y-\delta}$	metal oxide OSM
δ	off-stoichiometry of OSM
δ_O	off-stoichiometry of OSM after oxidation
δ_R	off-stoichiometry of OSM after reduction
n_{H_2O}	moles of water needed for oxidation per cycle
HHV_{H_2}	higher heating value of hydrogen
LHV_{H_2}	lower heating value of hydrogen
C_P^{OSM}	molar specific heat of the OSM
$C_P^{H_2O}$	molar specific heat of water
ΔH	change in enthalpy upon reduction

ΔS	change in entropy upon reduction
η	NRC chemical conversion efficiency
F_{Reheat}	energy factor for temperature change
F_{RXN}	energy factor for endothermic reduction
F_{Water}	energy factor for generating steam
F_{Pump}	energy factor for driving the vacuum pump
F_{Loss}	energy factor for heat leak
R_{TM}	ratio of inert reactor thermal mass to OSM thermal mass
$\dot{Q}_{Re-Rad}$	heat leak rate from re-radiation at the solar receiver
C_{H_2O}	extent of chemical conversion (ratio of water to hydrogen)
R_{H_2O}	ratio of water to hydrogen at reactor outlet during oxidation
K_{WS}	chemical equilibrium constant for water dissociation
$R_{\Delta H}$	ratio of ΔH to the change in enthalpy of water dissociation
η_{Pump}	efficiency of vacuum pump
T^o	reference temperature
P^o	reference pressure
R	gas constant
W_{Pump}^{Ideal}	ideal pump work
$W_{Friction}$	lost frictional work of vacuum pump
ΔH_{H_2O}	enthalpy of liquid water dissociation

Such a direct process has high theoretical efficiencies, but the requirement of temperatures above 2500 K (with gaseous product separations) limits its feasibility (Steinfeld, 2005). These two issues can be addressed by dividing the process into two or more separate reaction steps where the net reaction is water dissociation.

Hundreds of thermochemical cycles with varying numbers of reaction steps have been proposed and investigated for water splitting (Funk, 2001; Abanades et al., 2006; Funk and Reinstro, 1966). Among the most promising of these are two-step redox cycles, due to their simplicity and high theoretical efficiency (Steinfeld, 2005). A schematic illustration of a thermochemical two-step metal oxide redox cycle, revealing the relevant energy and mass balances, is shown in Fig. 1. Here, an intermediate oxygen storage material (OSM), such as a metal oxide, is first reduced at a high temperature, T_H (via Reaction (2)). The OSM is then cooled to a lower temperature, T_L, where it then re-oxidizes when exposed to steam (via Reaction (3)).

In the indicated cycle, a vacuum pump can be used to reduce the total pressure and oxygen partial pressure (P_{O_2}) to allow for the reduction of an OSM (Ermanoski et al., 2014; Venstrom et al., 2014). The energy input to

the system includes the work needed to drive the vacuum pump (W_{Pump}), the sensible heat needed to raise the temperature of the reactor and OSM from T_L to T_H (Q_{Reheat}), the energy needed to drive the endothermic reduction reaction (Q_{RXN}), along with the sensible and latent heat associated with generating the reactant steam (Q_{Water}). Note that by carrying out heat recuperation, some portion of the sensible heat removed from the reactor (Q_{Out}) and some portion of the sensible heat removed from the product stream during step two ($H_2 + H_2O$) can be recovered at an efficiency of ε_S and ε_G respectively. During the time required to complete both steps of the reaction (Δt), heat leaks from the system to the environment at a rate of $\dot{Q}_{Loss}$.

For the metal oxide ($M_xO_{y-\delta}$), δ_R and δ_O represent the off-stoichiometry (oxidation state) after steps one and two respectively. In Reaction (3), n_{H_2O} is the number of moles of water required to oxidize one mole of OSM from δ_R to δ_O at T_L. The units of $\delta_R - \delta_O$ can be taken as the moles of hydrogen produced per mole of OSM per cycle. For a two-step cycle, the OSM can be a pure or alloyed material undergoing partial reduction, or an arbitrary number of intermediate compounds or solution phases that absorb and release oxygen through reversible reactions (Meredig and Wolverton, 2011). Conceptually, one could