Title:

System efficiency for two-step metal oxide solar thermochemical hydrogen production, Part 1:
thermodynamic model and impact of oxidation kinetics

Authors:

B. D. Ehrhart ^a

C. L. Muhich ^a

I. Al-Shankiti ^{a,b}

A. W. Weimer ^{a*}

Abstract:

A comprehensive solar-to-hydrogen (STH) efficiency model, which includes the effect of oxidation kinetics, is developed for two-step solar thermochemical redox water splitting processing. Active materials flow through separate reduction and oxidation reactors. Two active redox materials are considered and compared in order to assess the impact of the rate of redox and the hydrogen productivity per cycle on STH efficiency. Reported oxidation rates for reduced cerium oxide (fast kinetics/lower H₂ productivity/cycle) and a ferrite/zirconia composite (slow kinetics/higher H₂ productivity/cycle) are used in the model in order to make a realistic comparison. Generally, the efficiency at thermodynamic equilibrium is higher for the ferrite/zirconia composite than ceria. Interactions between material specific parameters are compared, such as the combination of heat capacity and flow rate on sensible heating loads. Additionally, the sensitivity of oxidation kinetics on the overall cycle efficiency is illustrated. Model results show that kinetics can have a drastic effect on STH efficiency. Near-isothermal redox processing is more optimal for materials with slower kinetics, and especially with moderate to high gas heat recuperation. The kinetic effects are negligible for those active materials having fast oxidation rates, *i.e.* ceria, which benefit from a larger temperature difference (thermodynamic driving force) between the reduction and oxidation steps. This leads to different optimal operating conditions when oxidation kinetics are included in the analysis as compared to prior models when only thermodynamic equilibrium is considered.

Nomenclature

Greek Letters

α	Thermal absorptivity of solar receiver
δ	Extent of non-stoichiometry
ϵ	Thermal emissivity of solar receiver
ζ_{sun}	Solar flux at the earth's surface (W m^{-2})
η	Thermal efficiency
σ	Stefan-Boltzmann constant ($\text{W m}^{-2} \text{K}^{-4}$)
χ	Reaction conversion

Non-Greek Letters

A	Area (m^2)
C	Concentration ratio of solar collection area to receiver aperture area
C_P	Heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)
F_R	Fraction of reactive solid material
ΔG	Standard Gibbs free energy (J/mol)
h	Height that solid material must be raised during every cycle (m)
h_{eff}	Effective heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
ΔH	Enthalpy change (kJ/mol)
HHV_{H_2}	Higher heating value of hydrogen (MJ/kg)
k_B	Boltzmann constant (J/K)
$K_{\text{eq}}^{\text{WS}}$	Equilibrium constant of splitting water at the oxidation temperature
MW	Molecular weight of compound
N_A	Avogadro's Number (mol^{-1})
$\dot{n}$	Molar flow rate (mol/s)
n	Molar ratio or amount
p	Oxygen partial pressure (Pa)
P	Pressure (Pa)
$\dot{Q}$	Thermal energy flux (J/s)
Q	Thermal energy per mole of hydrogen produced (J/mol)
ΔS	Entropy change ($\text{J mol}^{-1} \text{K}^{-1}$)

t_{critical}	Time required to reach full conversion of oxidation reaction (s)
T	Temperature (K)
ΔT	Difference between reduction and oxidation temperatures (K)
x	Molar fraction

Sub-Scripts

A	Thermal energy at the solar receiver
amb	Ambient
AO	After oxidation
AR	After reduction
Aperture	At the solar receiver cavity aperture
AUX	Auxiliary
CONV	Convective
FIELD	Relating to the solar field
GG	Gas-gas
H2	Property or thermal energy relating to hydrogen
H2O	Property or thermal energy relating to water
HOX	Enthalpy of oxidation
HTR	Enthalpy of reduction
IC	Inert cooling
IH	Inert heating
io	Ratio of inert to oxygen
MECH	Mechanical
mix	Mixing
MOL	Energy related to producing one mole of hydrogen
O2	Property or thermal energy relating to oxygen
optic	Optical property of solar collector
OX	Oxidation
PUMP	Property or thermal energy of pump work
RED	Reduction
REJECT	Rejected thermal energy

RERAD	Thermal energy re-radiated from solar receiver
S	Reactive solids
SC	Solids cooling
SEP	Property or thermal energy of separation
SH	Solids heating
SOLAR	Solar thermal energy
SS	Solid-solid
STH	Solar-to-hydrogen
TC	Thermal energy available for thermochemical reaction
vap	Thermal energy of vaporization
wall	Property at wall of solar receiver
wh	Molar ratio of water to hydrogen
WS	Water splitting

Super-Scripts

°	Standard property
eff	Effective property
H2	Property or thermal energy relating to hydrogen
N2	Property or thermal energy relating to nitrogen
O2	Property or thermal energy relating to oxygen
R	Thermal energy to be rejected
Solid	Property or thermal energy relating to the reactive solids
Steam	Property or thermal energy relating to gaseous water (steam)
Water	Property or thermal energy relating to liquid water

1. Introduction

More than fifty million metric tons of hydrogen were produced in 2006, with expected increases of 10% per year [1]. In addition to processing fossil fuels and producing ammonia for fertilizer [1], H_2 is also a potentially useful transportation fuel, with ~ 2.5 times the specific energy content of gasoline [2] and automotive companies are currently releasing commercial models of hydrogen fuel cell cars [3]. However, H_2 is currently produced mainly via steam methane reforming [4], which inherently produces a minimum of 5.5 kg of CO_2 for each 1 kg of H_2 generated. Solar energy is one of the most widely available renewable energy sources [5] and could be used to generate H_2 . For solar driven water splitting processes, market adoption will ultimately depend on the cost of H_2 produced, which is dependent on many factors [6]. However, comparing process efficiency values can ignore price fluctuations, financing choices, and the legal environment in which projects are considered and give a more robust comparison between technological options. Of the solar water splitting processes currently under consideration, the simplest is running a conventional water electrolyzer using a photovoltaic cell. However, current photovoltaic and photo-chemical pathways only utilize a small portion of the available wavelengths of light and require multiple reaction steps and separations [5, 7], both of which can lower process efficiency and increase costs. Solar thermal processes use the entire solar spectrum and can operate with only one or two steps. This means that direct H_2 production via solar thermal processes can be much more efficient [8, 9]. In addition to a potential efficiency increase, but a similar process has been operated at the pilot scale [10]. Water can be solar thermally split directly into oxygen and hydrogen via thermolysis, but this requires very high temperatures ($\geq 2,273$ K) [8, 11]. To make water splitting more practical, a two-step thermochemical reaction cycle can be used. In these cycles, a metal oxide material is thermally reduced to produce oxygen. Steam is then passed over the reduced oxide to oxidize it, generating H_2 and reforming the original oxide.

Since the overall goal of thermochemical hydrogen production is to efficiently produce hydrogen from solar energy, the whole process must be analyzed to determine the effects of various parameters on the overall efficiency. Many researchers have attempted to calculate a theoretical STH efficiency, taking into account various heat sources, sinks, recycles, and different redox materials, and some have used entropy analysis [12, 13]. Even though the two-step thermochemical cycle is conceptually simple, there are many factors in such a process than

can be varied. Important factors that must be considered are the choice of the design conditions (temperature and pressure) for both the reduction and oxidation reactions, the method of oxygen removal from the reduction reaction, the heating of steam for the oxidation reaction, separation of the hydrogen product, and heat recuperation within the process [11].

Solar thermochemical water splitting efficiency calculations often use ceria as the active material [8, 14-17]. This is useful as ceria is currently one of the most promising materials available for solar thermochemical water splitting. However, the trends found for ceria may not necessarily hold for other materials. Some groups have attempted to incorporate other materials into efficiency models. Many groups [9, 18, 19] have used iron oxide in efficiency models. However, Diver *et al.* assumed complete conversion for both the reduction and oxidation reaction as well as using only the stoichiometrically required amount of steam [18], which are likely not realistic in an actual system. On the other hand, Singh *et al.* only considered energy requirements for reduction, rather than the process as a whole [19].

In addition to a constrained materials assessment, many efficiency models have focused on a cycle operating at thermodynamic equilibrium. This is seen as an upper bound on efficiency, as slower reaction rates only limit the achievable efficiency. Additionally, the achievable reaction rates are material and reactor design-dependent, making it difficult to use these analyses to explore general trends. Furler *et al.* have published the actual efficiency achieved by their experimental reactors [20]. This is certainly useful and necessary for the field as a whole, but not as useful for exploring a wide design space and investigating the impact of reaction rates of the system efficiency. Venstrom *et al.* have used an efficiency model using experimental data and extrapolated what efficiencies could be gained at a larger scale system [21]. Other groups have also discussed the impact of kinetics lowering the system efficiency, both chemical as well as heat and mass transport limitations [22-26].

In this work, we detail a thermodynamic model for the calculation of overall STH efficiency. Specifically, we expand on previous work by offering new insights from a material besides the commonly-used ceria, including showing what factors become more or less important with a different material. Further, this work includes oxidation kinetics for both materials in a general way rather than using experimental data directly to examine the impact of kinetics on both system efficiency and the identification of ideal operation points.

2. Methods

The STH efficiency is calculated using a system normalized to producing 1 mole of H_2 . This model is meant to illustrate trends within a solar thermochemical water splitting system by examining the influence of different parameters on system losses that are un-avoidable and necessary to operation of the system. A real system will have a number of other trade-offs and energy losses, meaning that a real system will likely have lower efficiency values than those reported here. Below, the thermodynamic model will be described in detail. Oxidation kinetics will then be included and the method for applying them to the thermodynamic model will be described. Finally, details will be given for all model derivations, inputs, and calculations in order to provide a guide for future work.

2.1. Efficiency Calculations for Thermodynamic Equilibrium

The model consists of temporal heat fluxes into and out of the system and heat flows within the system that are normalized to the production of a single mole of hydrogen. The system models ceria and a ferrite/zirconia composite as the active materials, and a description of the thermodynamics of these materials is included. The model assumes that a recycled inert sweep gas is used to maintain a low O_2 partial pressure for the reduction reaction and that excess steam is used for oxidation. Heat recuperation for both of these gaseous streams is included, as well as solid heat recuperation for the active materials. Equations for all of these heat flows will be given explicitly, as well as any constants used.

2.1.1. Overall System Description

We consider an overall process, as shown in Figure 1, in which concentrated solar energy drives a two-step metal oxide thermal reduction and oxidation reaction cycle. A continuous process is assumed in which reactive material flows around a process to avoid batch operation [27-29]. Filled block arrows denote thermal temporal fluxes, while empty block arrows represent heat flows normalized per mole of H_2 . The thermal source of each of the intra-system thermal requirements (empty block arrows) is assumed to either come from an intra-system heat benefit or the thermal flux available for thermochemical reaction ($\dot{Q}_{TC}$), while the thermal sink for each of these requirements is the associated unit operation or stream that the empty arrow indicates. Similarly, empty block arrows for the intra-system heat benefits point from the heat source out

$$\frac{1}{\Delta\delta} M_y O_{x-\delta_{OX}} \rightarrow \frac{1}{\Delta\delta} M_y O_{x-\delta_{RED}} + \frac{1}{2} O_2 \quad (1)$$

$$\frac{1}{\Delta\delta} M_y O_{x-\delta_{RED}} + H_2 O \rightarrow \frac{1}{\Delta\delta} M_y O_{x-\delta_{OX}} + H_2 \quad (2)$$

However, not all solar thermochemical water splitting materials operate via an O-vacancy reaction mechanism, such as ferrites. For these metal oxides, analogous expressions can be written using the overall conversion of the reactants, χ . This is based on a generic metal oxide, $M_y O_x$, undergoing a stoichiometric reduction and oxidation cycle, such as one shown in Equation (3).

$$M_y O_x \rightarrow (1 - \chi_{RED}) M_y O_x + \chi_{RED} \frac{y}{x - y} MO + \frac{\Delta\chi}{2} O_2 \quad (3)$$

Based on this general equation, the reduction and oxidation cycle can be re-written in an analogous way to Equations (1) and (2), where the oxidation reaction does not necessarily fully re-oxidize the material to $M_y O_x$, but rather to some mixture of $M_y O_x$ and MO . These expressions are given in Equations (4) and (5). For the remainder of the discussion, $\Delta\delta$ will be used, but the analogous $\Delta\chi$ expression could also be used.

$$\frac{1 - \chi_{OX}}{\Delta\chi} M_y O_x + \frac{\chi_{OX}}{\Delta\chi} \frac{y}{x - y} MO \rightarrow \frac{1 - \chi_{RED}}{\Delta\chi} M_y O_x + \frac{\chi_{RED}}{\Delta\chi} \frac{y}{x - y} MO + \frac{1}{2} O_2 \quad (4)$$

$$\frac{1 - \chi_{RED}}{\Delta\chi} M_y O_x + \frac{\chi_{RED}}{\Delta\chi} \frac{y}{x - y} MO + H_2 O \rightarrow \frac{1 - \chi_{OX}}{\Delta\chi} M_y O_x + \frac{\chi_{OX}}{\Delta\chi} \frac{y}{x - y} MO + H_2 \quad (5)$$

To calculate the $\Delta\delta$ value, the thermodynamic extent of reduction is determined for both the reduced and oxidized state of the material at the reduction and oxidation temperature and pressure conditions of interest. For ceria, the model from Bulfin *et al.* [17] is used, which utilizes data from Panlener *et al.* [30]. For the ferrite zirconia mixture, calculations were performed using the FactSage thermodynamic prediction software[31] for a 20%-wt. $CoFe_2O_4$ mixed with ZrO_2 ; the results of these thermodynamic predictions are shown in Section S.1 of the Supplemental Material. To calculate the extent of reduction of the material in the reduced state, the reduction temperature is used in conjunction with the reduction pressure as the partial pressure of oxygen.

To calculate the extent of reduction of the oxidized material, the oxidation temperature is used along with the equilibrium partial pressure of oxygen at the oxidation temperature and overall pressure (1 atm) due to water thermolysis (p_{Ox}). The water thermolysis equilibrium values were also calculated using the FactSage thermodynamic prediction software. Details and results of the FactSage calculations for oxygen partial pressure based on water thermolysis can be found in Section S.2 of the Supplemental Material.

2.1.3. Overall System Efficiency

The overall STH efficiency is defined as the ratio of the chemical energy in hydrogen (using the higher heating value, HHV) to the amount of earth-incident solar energy required to produce that hydrogen by the proposed process. This relationship is shown in Equation (6), where η_{STH} is the STH efficiency, $\dot{n}_{\text{H}_2}$ is the molar flow rate of hydrogen, HHV_{H_2} is the higher heating value of hydrogen ($286.61 \text{ kJ/mol} = 142.18 \text{ MJ/kg}$ [32]), and $\dot{Q}_{\text{SOLAR}}$ is the amount of solar energy per unit time incident on the concentrating mirrors.

$$\eta_{\text{STH}} = \frac{\dot{n}_{\text{H}_2} \text{HHV}_{\text{H}_2}}{\dot{Q}_{\text{SOLAR}}} \quad (6)$$

The molar flow rate of hydrogen is calculated from the thermal power available for the thermochemical reaction, $\dot{Q}_{\text{TC}}$, and the amount of thermal energy needed to produce a single mole of hydrogen, Q_{MOL} (see Equation (7)). This analysis assumes a single mole of H_2 , and this will be discussed further below.

$$\dot{n}_{\text{H}_2} = \frac{\dot{Q}_{\text{TC}}}{Q_{\text{MOL}}} \quad (7)$$

2.1.4. Solar Energy Fluxes

The relationship between the solar energy, $\dot{Q}_{\text{SOLAR}}$, and thermal energy available for hydrogen production, $\dot{Q}_{\text{TC}}$, depends on the heat absorbed by the receiver/reactor, the losses associated with re-radiation, and the efficiency of the solar field which collects and concentrates the incident sunlight; these values are calculated using Equations (8), (10), and (12). These energy flows and losses depend heavily on the exact receiver/reactor design and materials of construction. Because this report is meant to be a general analysis, these losses are simplified, as detailed below. The thermal energy available for the thermochemical reaction, $\dot{Q}_{\text{TC}}$, is calculated from the effective

thermal absorptivity of the solar receiver/reactor α (taken to be 0.95), the thermal energy flux at the receiver ($\dot{Q}_A$), the amount of energy flux lost due to re-radiation ($\dot{Q}_{RERAD}$), and convection ($\dot{Q}_{CONV}$) as shown in Equation 8. The heat not absorbed by the receiver ($\dot{Q}_{NA}$) is rejected from the system, and is calculated in Equation (9). Conduction losses are not considered in this analysis and neither are convective or radiative losses for the non-aperture receiver area, as these are typically small for a well-insulated receiver[8, 33] and are typically excluded in these types of analyses [8, 14, 15, 34]. These assumptions enable the calculation of an upper limit on system efficiency without assuming a particular receiver/reactor configuration.

$$\dot{Q}_{TC} = \alpha \cdot \dot{Q}_A - \dot{Q}_{RERAD} - \dot{Q}_{CONV} \quad (8)$$

$$\dot{Q}_{NA} = (1 - \alpha)\dot{Q}_A \quad (9)$$

The solar thermal energy at the receiver aperture ($\dot{Q}_A$) is determined by the solar flux incident on the heliostats and the optical efficiency of the collecting reflectors (η_{optic}). This optical efficiency is taken to be 89.3%, based on a single reflection from a reflective surface with an ideal reflectivity of 94% and an average cleanliness factor of 95% [35]. It should be noted that only optical losses are considered here, as these are both generally applicable and unavoidable in concentrated solar thermal systems. By contrast, losses from blocking and shading, cosine effects, atmospheric attenuation, and mirror misalignment are not considered here. Many of these losses depend greatly on specific field/dish arrangements, geographical location, time of day, time of year, and mirror design. Thus, this analysis is an upper limit on efficiency for the exploration of various trends, rather than an estimation of specific values achievable in a real system. The equation for determining $\dot{Q}_A$ is shown in Equation (10). The corresponding amount of solar energy lost due to optical inefficiencies ($\dot{Q}_{FIELD}$) is the amount of energy not reflected with the optical efficiency η_{optic} , and is shown in Equation (11).

$$\dot{Q}_A = \eta_{optic}\dot{Q}_{SOLAR} \quad (10)$$

$$\dot{Q}_{FIELD} = (1 - \eta_{optic})\dot{Q}_{SOLAR} \quad (11)$$

The amount of solar energy hitting the solar collectors depends on the solar flux at the earth's surface ($\zeta_{sun} = 1,000 \text{ W/m}^2$) and the total reflective area of the heliostat field or other reflective area, such as a parabolic dish, (A_{field}) as shown in Equation (12). This reflective area of the field

can be thought of as an effective reflective area, since mirrors may block and shade one another as well as a variety of other losses that occur when collecting and concentrating solar thermal energy, as outlined above. However, these losses are not explicitly accounted for in this analysis, and so care must be used if these results are compared to other analyses that do take these losses into account explicitly.

$$\dot{Q}_{SOLAR} = \zeta_{sun} A_{field} \quad (12)$$

The reflective area of the collectors is directly related to the flow rate of product hydrogen, but in this analysis has no direct effect on the final efficiency. This is because the current analysis is based on the production of a single mole of hydrogen in the Q_{MOL} term described below. The solar energy flow rate terms ($\dot{Q}_{SOLAR}$, $\dot{Q}_A$, *etc.*) scale the reflective area directly with the flow rate of hydrogen because Equation (7) can be re-arranged to obtain an expression for the ratio of $\dot{n}_{H_2}/A_{field}$, which is a constant. In an actual system this does not hold true and cosine, attenuation, and alignment losses increase with increasing size of the heliostat field.

The losses due to re-radiation at the receiver ($\dot{Q}_{RERAD}$) are determined by Equation (13), which includes the thermal emissivity of the receiver (ϵ , assumed to be 0.95), the Stefan-Boltzmann constant ($\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$), the temperature of the reactor wall (T_{wall}), and the aperture area ($A_{aperture}$). This simplified and optimistic estimation of radiative losses based on a simple cavity aperture area is meant to be a general estimation rather than based on a calculation of a specific system. The area of the aperture is given by the reflective area of the solar field (A_{field}) and the concentration ratio ($C = A_{field}/A_{aperture}$). Here the concentration ratio is assumed to be 3,000. The temperature at the outer wall of the receiver (T_{wall}) is assumed to be 20 K above the reduction temperature.

$$\dot{Q}_{RERAD} = \epsilon \sigma A_{aperture} T_{wall}^4 \quad (13)$$

Convective losses ($\dot{Q}_{CONV}$) are determined by a lumped heat transfer parameter (h_{eff}), the area of the cavity receiver aperture ($A_{aperture}$), and the difference between the temperature at the receiver wall (T_{wall}) and the ambient temperature ($T_{amb} = 298 \text{ K}$). A more rigorous calculation for convective losses would need to take specific cavity interior dimension into account in addition to the dimensions of the aperture, but this simplified form allows for convective losses to be approximated and to scale with both temperature and aperture size. The effective heat transfer

coefficient is estimated from Falcone [33], includes both natural and forced convection, and is scaled to relate to the aperture area rather than the interior absorber area. The value of h_{eff} is estimated to be $48.2 \text{ W m}^{-2} \text{ K}^{-1}$.

$$\dot{Q}_{\text{CONV}} = h_{\text{eff}} A_{\text{aperture}} (T_{\text{wall}} - T_{\text{amb}}) \quad (14)$$

2.1.5. Thermal Energy Required to Produce Hydrogen

The energy required to produce a single mole of hydrogen (Q_{MOL}) is determined by the thermal reduction endotherm of the solid material ($Q_{\text{HTR}} = \Delta H_{\text{RED}}$), the energy needed to heat the material from the oxidation temperature to the reduction temperature (Q_{SH}), the energy required to heat the inert gas from the inert gas separation temperature to the reduction temperature (Q_{IH}), and other auxiliary heating requirements (Q_{AUX}), as shown in Equation (15). The values for ΔH_{RED} and C_P for both ceria and the ferrite/zirconia are shown in Table 1.

$$Q_{\text{MOL}} = Q_{\text{HTR}} + Q_{\text{SH}} + Q_{\text{IH}} + Q_{\text{AUX}} \quad (15)$$

Table 1: Reduction endotherms and heat capacity for reactive solid materials. The references for the ceria values are shown in the table. The values for the ferrite/zirconia composite were estimated using FACTSageTM.

Material	ΔH_{RED} [kJ/(1/2 mol O ₂)]	C_P [J mol ⁻¹ K ⁻¹]
CeO ₂	480 [36]	80 [34]
20 %-wt CoFe ₂ O ₄ on ZrO ₂	309	187.9

The energy required to heat the solid from the oxidation to the reduction temperature (Q_{SH}) is given in Equation (16). This incorporates the heat capacity of the solid (C_P^{solid}), the difference between the reduction and oxidation temperatures (ΔT), the solid-solid heat recuperation effectiveness (ε_{SS}), and the quantity of material necessary to produce one mole of H₂, which is accounted for by the extent of reaction ($\Delta\delta$) from Equation (1), and the fraction of solid material that is thermochemically active (F_R). The fraction of solid material that is thermochemically active (F_R) denotes how much of the solid material that must be heated is active rather than an inert support or binder material, which does not contribute towards the thermochemical reaction but still must be heated.

$$Q_{\text{SH}} = \frac{C_P^{\text{solid}}}{F_R \Delta\delta} \Delta T (1 - \varepsilon_{\text{SS}}) \quad (16)$$

2.1.6. Auxiliary Heating Requirements and Benefits

The auxiliary heating requirement includes terms deleterious to the overall efficiency including: water heating requirements (Q_{H_2O}), heat equivalent of pump work (Q_{PUMP}), heat equivalent of mechanical work needed for reactor operation (Q_{MECH}), heat equivalent of separations work needed (Q_{SEP}); and terms beneficial to the overall efficiency including: oxidation exotherm (Q_{HOX}), the un-recuperated heat in the solid flow as it cools (Q_{SC}), the un-recuperated heat of the inert gas (if any) as it cools (Q_{IC}), and the sensible heat from the oxygen stream from the reduction reaction (Q_{O_2}). The overall auxiliary heating equation is calculated by Equation (17).

$$Q_{AUX} = (Q_{H_2O} + Q_{PUMP} + Q_{MECH} + Q_{SEP}) - (Q_{HOX} + Q_{SC} + Q_{IC} + Q_{O_2}) \quad (17)$$

This is an optimistic simplification, as heat recuperation is not always realistic even when possible. There is no specific determination of what heating benefit will heat what specific heating requirement in the equation above; rather, the heat requirements and benefits that are possibly able to interact are compared. This analysis considers what is possible to achieve without assuming a particular system design in order to examine more general trends. Q_{AUX} is set to a value of zero if the initial calculated Q_{AUX} value is negative, and this excess heat (Q_{AUX}^{REJ}) is rejected from the system. It should be noted that Q_{AUX} can never be negative, as explained by Ermanoski *et al.*[34]. This is because the heating benefits (Q_{HOX} , Q_{SC} , and Q_{O_2}) will reject heat at a temperature near the oxidation temperature, and therefore cannot contribute to the heating requirements at the reduction temperature (Q_{SH} , Q_{IH} , and Q_{HTR}). The oxidation exotherm is given by subtracting the heat of combustion of hydrogen ($\Delta H_{c,H_2} = 286 \text{ kJ/mol}$) from the reduction exotherm, $Q_{HOX} = \Delta H_{RED} - \Delta H_{c,H_2}$. The other terms are described in more detail below.

The water heating requirements (Q_{H_2O}) are calculated in Equation (18) and include two terms: water heating ($Q_{H_2O}^{heat}$), and heat recuperation from the steam and hydrogen mixture as it cools ($Q_{H_2O}^{cool}$). The water heating term ($Q_{H_2O}^{heat}$) is the energy necessary to heat the calculated amount of water required for oxidation from a liquid phase at ambient temperature to steam at the oxidation temperature. The steam/hydrogen cooling term ($Q_{H_2O}^{heat}$) is the sensible heat released from the cooling of the one mole of hydrogen formed and the excess water from the oxidation temperature to ambient. This term is then discounted by the heat recuperation effectiveness (ϵ_{GG}). These expressions incorporate the specific heat capacity at constant pressure

(C_P) of liquid water, steam, and hydrogen; the molecular weight (MW) of water; and the latent heat of vaporization of water to steam (ΔH_{vap}). The heat capacities are all taken from the NIST Chemistry WebBook [37]. The amount of water required for reaction is given by n_{wh} , which is a ratio of the number of moles of water to 1 mole of hydrogen after oxidation is complete; this is explained below. The un-recuperated heat of the water/steam mixture ($Q_{\text{H}_2\text{O}}^{\text{REJ}}$) which is rejected to ambient as it cools is equal in magnitude to $Q_{\text{H}_2\text{O}}$, and is shown explicitly in Equation (19). Specifics of how the water/hydrogen heating and cooling terms are calculated are given in Section S.3 of the Supplemental Material.

$$Q_{\text{H}_2\text{O}} = Q_{\text{H}_2\text{O}}^{\text{heat}} - \varepsilon_{\text{GG}} Q_{\text{H}_2\text{O}}^{\text{cool}} \quad (18)$$

$$Q_{\text{H}_2\text{O}}^{\text{REJ}} = Q_{\text{H}_2\text{O}}^{\text{heat}} - \varepsilon_{\text{GG}} Q_{\text{H}_2\text{O}}^{\text{cool}} \quad (19)$$

We assume that the steam and solids are in a well-mixed, counter-flow arrangement that reaches thermodynamic equilibrium at each infinitesimal point along the length of contact. The ratio of excess steam to generated hydrogen (n_{wh}) is calculated by re-arranging the equilibrium constant of the net water splitting reaction ($K_{\text{eq}}^{\text{WS}}$), as shown in Equation (20). This includes the standard enthalpy of water splitting ($\Delta H_{\text{WS}}^\circ = 250.8 \text{ kJ/mol}$) and the standard entropy of water splitting ($\Delta S_{\text{WS}}^\circ = 57.35 \text{ J mol}^{-1} \text{ K}^{-1}$) both on a steam basis [34]. The partial pressure of oxygen (p_{AO}) is then found by calculating the equilibrium partial pressure of oxygen of the reduced material at the oxidation temperature. The value of n_{wh} typically varies greatly depending on the operating conditions for reduction and oxidation being used. An example of the range of n_{wh} values for an example calculation is given in Section S.4 of the Supplemental Information.

$$K_{\text{eq}}^{\text{WS}} = \exp\left(-\frac{\Delta G_{\text{WS}}^\circ}{RT_{\text{OX}}}\right) = \exp\left(-\frac{\Delta H_{\text{WS}}^\circ - T_{\text{OX}}\Delta S_{\text{WS}}^\circ}{RT_{\text{OX}}}\right) = \frac{n_{\text{H}_2} n_{\text{O}_2}^{1/2}}{n_{\text{H}_2\text{O}}} = \frac{\sqrt{p_{\text{AO}}}}{n_{\text{wh}}} \quad (20)$$

The pump work term (Q_{PUMP}) is only used for a system operating under vacuum for the reduction reaction. This is not considered here, but explored in a subsequent analysis [38]. In this analysis, Q_{PUMP} is set to zero.

The mechanical heat requirements, shown in Equation (21), are the heat-equivalent of the work required to move the solids within the reaction system. It should be noted that this term is particularly dependent on the reactor design used, and so the form of this term can vary widely.

For this work, it is assumed that the solid materials are raised some distance h for each cycle, taken to be 10 meters in this analysis. This term is inflated by $\eta_{MECH} = 10\%$, which converts useful mechanical work to the heat equivalent. This lumped efficiency term includes thermal-to-electricity conversion, electric-to-pump/motor efficiency, and an estimation of the conversion of pump/motor work-to-useful work done on the solid materials (such as frictional losses for a mechanically driven system or pressure drop losses for a fluidized bed-type system). This mechanical work involves a conversion to heat equivalent, and so the heat rejected in this conversion (Q_{MECH}^{REJ}) is calculated in Equation (22).

$$Q_{MECH} = \frac{MW_{solid}gh}{F_R \Delta \eta_{MECH}} \quad (21)$$

$$Q_{MECH}^{REJ} = (1 - \eta_{MECH})Q_{MECH} \quad (22)$$

The overall separations work is a combination of the separations work for water/hydrogen (after oxidation) and inert/oxygen (after reduction), $Q_{SEP} = Q_{SEP}^{O_2} + Q_{SEP}^{H_2}$. The separations work for the water/hydrogen separation ($Q_{SEP}^{H_2}$) is based on an estimation of the heat-equivalent of the work required to separate the hydrogen product from the excess water, and is shown in Equation (24). This is based on the 2nd Law of Thermodynamics ($\Delta Q = T \Delta S$), which is then inflated by an assumed separation efficiency, $\eta_{SEP}^{H_2} = 15\%$. The entropy of mixing (ΔS_{mix}) for each stream (feed into separator, product stream out of separator, and effluent stream out of separator) is given in Equation (23), where x is the molar fraction of hydrogen in the stream and n is the molar flow rate of that stream. Finally, it is assumed that the final product stream has a purity of 99.9% hydrogen, while the effluent stream has an equilibrium-determined amount of hydrogen dissolved in it (1.4×10^{-5} mole H_2 per mole H_2O at 298 K, from the NIST Chemistry WebBook [39]). The thermodynamic separation is done at the water/hydrogen separation temperature, $T_{SEP}^{H_2}$, here assumed to be 373 K (100°C). This separation work involves a conversion to heat equivalent, and so the heat rejected in this conversion ($Q_{SEP}^{H_2, REJ}$) is calculated in Equation (25).

$$\Delta S_{mix} = -N_A k_B n [x \ln(x) + (1 - x) \ln(1 - x)] \quad (23)$$

$$Q_{SEP}^{O_2} = \frac{T_{SEP}^{O_2}}{\eta_{SEP}^{O_2}} (\Delta S_{mix}^{product} + \Delta S_{mix}^{effluent} - \Delta S_{mix}^{feed}) \quad (24)$$

$$Q_{SEPH_2}^{REJ} = (1 - \eta_{sep}^{H_2}) Q_{SEP}^{H_2} \quad (25)$$

2.1.7. Recycled Inert Gas Terms

This analysis assumes that a counter-flow recycled inert gas sweep is used for the reduction reaction. A similar method as Ref [14] is used to calculate the amount of inert gas (assumed to be nitrogen) required. We assume a counter-flow inert gas/solids arrangement, and we assume that each infinitesimal point along the solid/gas contact reaches local thermodynamic equilibrium. The amount of inert gas required is calculated as a ratio of moles of inert gas per mole of oxygen (n_{io}), as shown in Equation (26). Here, p_{AR} is the oxygen partial pressure in the inert sweep gas stream after reduction, P_{RED} is the total pressure of the reduction zone ($P_{RED} = 1 \text{ atm} = 101,325 \text{ Pa}$ for the inert gas sweep case), and p_{RED} is the oxygen partial pressure of the solid stream after reduction. This equation compares the amount of oxygen produced by determining the oxygen content of the inert gas stream before and after reduction, then calculating how much inert gas is needed to achieve that level of dilution. p_{AR} is obtained by calculating the equilibrium oxygen partial pressure above the reactive solids that are at the reduction temperature (T_{RED}) and the oxidized stoichiometric state (δ_{OX}). It should be noted that the validity of this method of calculating inert gas flow (as well as other inert gas assumptions) will be discussed in subsequent analyses [38, 40]. An example of the range of n_{io} values for an example calculation is given in Section S.4 of the Supplemental Information.

$$n_{io} = \left(\frac{p_{AR}}{P_{RED} - p_{AR}} - \frac{p_{RED}}{P_{RED} - p_{RED}} \right)^{-1} \quad (26)$$

The separation work of the inert gas and oxygen ($Q_{SEP}^{O_2}$) is shown in Equation (27), where $T_{SEP}^{O_2}$ is the oxygen/inert gas separation temperature (assumed to be $1,223 \text{ K} = 950 \text{ }^\circ\text{C}$), $\eta_{SEP}^{O_2}$ is the oxygen/inert separation efficiency (assumed to be 10%), and ΔS_{mix} is the entropy of mixing of each sub-stream (general equation shown in Equation (23)). The mole fractions are calculated using the oxygen partial pressures that were used to calculate n_{io} (Equation (26)). Realistic practical values for many of these parameters are unknown, and so a more thorough examination

of the sensitivity of these values has been carried out in Ref [38]. An oxygen product purity after separation of 100% was assumed for this closed system, and the oxygen partial pressure for reduction (p_{RED}) was used to determine the final effluent oxygen concentration. This separation work involves a conversion to heat equivalent, and so the heat rejected in this conversion (Q_{SEPO2}^{REJ}) is calculated in Equation (28).

$$Q_{SEP}^{O_2} = \frac{T_{SEP}^{O_2}}{\eta_{SEP}^{O_2}} (\Delta S_{mix}^{product} + \Delta S_{mix}^{effluent} - \Delta S_{mix}^{feed}) \quad (27)$$

$$Q_{SEPO2}^{REJ} = (1 - \eta_{SEP}^{O_2}) Q_{SEP}^{O_2} \quad (28)$$

In addition to the energy required to purify the recycled inert gas, the inert gas must be heated to the reduction temperature. This sensible heating requirement is calculated in Equation (29), where ε_{GG} is the gas heat recuperation effectiveness, n_{io} is the inert-to-oxygen molar ratio, $T_{SEP}^{O_2}$ is the oxygen/inert separation temperature (here assumed to be 950 °C = 1,223 K), T_{RED} is the reduction temperature, and $C_P^{N_2}$ is the specific heat capacity of nitrogen gas, which is the assumed inert gas. The factor of 1/2 applied to the n_{io} ratio is to account for that fact that 1/2 moles of oxygen are produced per 1 mole of hydrogen. The specific heat capacity of nitrogen is obtained from the NIST Chemistry WebBook [37]. This term is not included in the auxiliary heating requirements (Q_{AUX}), but rather in the Q_{MOL} term. This is because the heat required is typically (though not necessarily) at or above the oxidation temperature (T_{OX}), and so will not benefit from any potential heat benefit terms in Q_{AUX} .

$$Q_{IH} = (1 - \varepsilon_{GG}) \frac{n_{io}}{2} \int_{T_{SEP}^{O_2}}^{T_{RED}} C_P^{N_2}(T') dT' \quad (29)$$

2.1.8. Heat Benefits

There are also a number of heat benefits within the system. In addition to the oxidation exotherm (Q_{HOX}) as a heat benefit to Q_{AUX} , the un-recuperated heat in the solid reactive material as it cools down (Q_{SC}) is also a thermal credit. This credit is equal in magnitude to the un-recuperated heat required to heat the solids (Equation (16)); the only difference is that Q_{SC} is the un-recuperated heat of the solids as they cool, whereas Q_{SH} is the un-recuperated heat of the solids as they are heated. The equation for Q_{SC} is shown in Equation (30).

$$Q_{SC} = \frac{C_p^{solid}}{F_R \Delta \delta} \Delta T (1 - \varepsilon_{SS}) \quad (30)$$

There is also a sensible heat benefit from the inert gas as it cools from the reduction temperature to the separation temperature. This heat is especially useful, as all of this heat is at temperatures somewhere between the relatively high oxygen separation temperature ($T_{SEP}^{O_2}$) and the even higher reduction temperature (T_{RED}). This heat benefit is equal in magnitude to the inert gas sensible heat requirement (Equation (29)), and is shown in Equation (31) for completeness. This term is included in Q_{AUX} because, while the inert/oxygen separation temperature is high, it can be at or below the oxidation temperature.

$$Q_{IC} = (1 - \varepsilon_{GG}) \frac{n_{io}}{2} \int_{T_{SEP}^{O_2}}^{T_{RED}} C_p^{N_2}(T') dT' \quad (31)$$

Finally, the sensible heat credit from the oxygen is shown in Equation (32). This includes the specific heat capacity of oxygen ($C_p^{O_2}$), the amount of oxygen ($n_{O_2} = 0.5$ moles), and the difference between the reduction and ambient temperatures (T_{red} and T_{amb}). The entire temperature from reduction to ambient is considered, because the 0.5 moles of oxygen are cooled over that entire range, even though there is a separation step somewhere within that range. Sensible heat could be recovered both above and below the separation temperature. The heat capacity of oxygen is given by the NIST Chemistry WebBook [37].

$$Q_{O_2} = n_{O_2} \int_{T_{amb}}^{T_{RED}} C_p^{O_2}(T') dT' \quad (32)$$

2.1.9. Heat Rejection

The system boundary shown in Figure 1 includes a number of rejected heat fluxes. Most of these fluxes originate from the solar field and receiver, as described above, but there is also the heat rejected from the thermochemical process that produces one mole of H_2 : $\dot{Q}_{REJ}^{MOL}$. This heat rejection flux is calculated in Equation (33), and includes heat rejection from the near-ambient steam cooling ($Q_{H_2O}^{REJ}$), heat not able to be used by auxiliary terms (Q_{AUX}^{REJ}), as well as rejected heat from the conversion from heat to useful work for mechanical motion (Q_{MECH}^{REJ}), pump work (Q_{PUMP}^{REJ}), and separation ($Q_{SEP}^{REJ} = Q_{SEPO_2}^{REJ} + Q_{SEPH_2}^{REJ}$). Thus, the total heat

rejected from the system ($\dot{Q}_{REJECT}$) is calculated in Equation (34) and consists of all of the heat fluxes from both the solar field, solar receiver, and thermochemical process. The total heat input to the system ($\dot{Q}_{IN}$, Equation (35)) and the total heat output from the system ($\dot{Q}_{OUT}$, Equation (36)) differ by only 0.0004% of $\dot{Q}_{IN}$. This small discrepancy in the model is due to the difference between temperature and pressure conditions of the H₂O input/reactant stream and the H₂ and O₂ output/product streams, and the mismatch associated with the standard conditions assumed in the HHV value.

$$\dot{Q}_{REJ}^{MOL} = \dot{n}_{H_2} (Q_{H_2O}^{REJ} + Q_{AUX}^{REJ} + Q_{MECH}^{REJ} + Q_{PUMP}^{REJ} + Q_{SEP}^{REJ}) \quad (33)$$

$$\dot{Q}_{REJECT} = \dot{Q}_{FIELD} + \dot{Q}_{NA} + \dot{Q}_{RERAD} + \dot{Q}_{CONV} + \dot{Q}_{REJ}^{MOL} \quad (34)$$

$$\dot{Q}_{IN} = \dot{Q}_{SOLAR} \quad (35)$$

$$\dot{Q}_{OUT} = \dot{n}_{H_2} HHV_{H_2} + \dot{Q}_{REJECT} \quad (36)$$

2.2. Kinetic Limitations

Kinetic limitations are taken into account by determining the relative extents of reaction at the reaction rates at a given oxidation temperature and the highest possible oxidation temperature, *i.e.* the isothermal operation temperature. This is done by calculating the time ($t_{critical}$) required to reach full conversion (> 0.999) of the oxidation reaction at the highest oxidation temperature considered ($\Delta T = 0$) using existing kinetic models of solar thermochemical water splitting oxidation. For each oxidation temperature lower than the maximum temperature ($\Delta T > 0$), the reaction conversion is found for the same oxidation time ($t_{critical}$). This extent of conversion is then multiplied by the thermodynamic efficiency to calculate the kinetic-corrected efficiency. We use the kinetic model of cerium oxide and ferrite/zirconia as determined by Arifin [41] and Scheffe *et al.*[42], respectively. Details of these expressions, as well as an example calculation, are given in Section S.5 of the Supplemental Material.

2.3. Calculation and Analysis

Using the expressions described above, a computer code was written and executed using the MATLAB computing language and software (MATLAB Release 2015a, The MathWorks, Inc., Natick, Massachusetts, United States). A single value was evaluated for both the reduction temperature (T_{RED}) and pressure (p_{RED}), as many others [14, 16, 34, 43, 44] have considered the

effects of these parameters on efficiency, and generally find that increasing the reduction temperature increases STH efficiency. A range of oxidation temperature (T_{OX}) were considered, and are directly related to T_{RED} by the temperature difference between reduction and oxidation ($\Delta T = T_{\text{RED}} - T_{\text{OX}}$). Because T_{RED} is constant, as ΔT increases, T_{OX} decreases ($T_{\text{OX}} = T_{\text{RED}} - \Delta T$). A T_{RED} of 1,600 K with ΔT values of 0 to 250 K (step size of 10 K) were considered for the ferrite/zirconia composite in order to avoid issues with the thermodynamic predictions for the ferrite at higher temperatures, such as slag formation and volatilization. The same temperatures are considered for ceria in order to make more direct comparisons between the two materials. A reduction partial pressure for oxygen of 0.1 Pa was used, though alternate partial pressures are considered elsewhere [38]. Only a single value of $F_R = 1$ (100% active material) is considered, as the addition of inert solid material will decrease efficiency in a predictable way. Solid-solid heat recuperation efficiencies (ϵ_{SS}) and gas-gas heat recuperation efficiencies (ϵ_{GG}) from 0-100% were included to illustrate bounds on the possible effects of these parameters; additional analysis of the impact of these factors on the system efficiency is given in Ref [40]. A full set of example calculations are given in Section S.6 of the Supplemental Information listing conditions, constants, and calculated values for all major terms in the efficiency calculations. Additionally, while the main focus of this work is on the thermochemical process rather than the solar field and receiver performance, a summary of various efficiency terms to show the relative performance of the field, receiver, and thermochemical parts of the plant are shown in Section S.7 of the Supplemental Information.

3. Results

System efficiency values for both ceria and ferrite/zirconia active redox materials are shown here. These values include comparisons to work by others on similar efficiency models. Differences between the ceria and ferrite/zirconia efficiency are shown. The effect of oxidation kinetics are then illustrated and shown for both materials.

3.1. Thermodynamic Efficiency of Ceria and Ferrite/Zirconia Cycles

Efficiency values for both ceria and the ferrite/zirconia composite are shown in Figure 2a and b respectively for various values of gas heat recuperation effectiveness.

a)

b)

Figure 2: Solar-to-hydrogen efficiency for a) ceria and b) ferrite/zirconia active redox materials at various levels of gas heat recuperation (ϵ_{GG}) and a reduction temperature of 1,600 K, a reduction pressure of 0.1 Pa, and a solid heat recuperation effectiveness of 50%.

Generally, the efficiency values for ceria are consistent with previous efficiency analyses using ceria [14-16, 34]. They show an increasing efficiency with increasing ΔT up to an optimum, then the efficiency value decreases. However, the efficiency of the ferrite/zirconia system behaves quite differently. The STH efficiency increases monotonically up to $\Delta T = 250$ K.

a)

b)

Figure 3: Heat loads and benefits for a) ceria and b) ferrite/zirconia active redox materials with gas heat recuperation of 90%, a reduction temperature of 1,600 K, a reduction pressure of 0.1 Pa, and a solid heat recuperation effectiveness of 50%.

The reason for this discrepancy between the shape of the efficiency curves between ceria and ferrite/zirconia stem from the various heat requirements as shown in Figure 3. The main difference in the shapes of the efficiency curves is the behavior of the Q_{AUX} term. The slope of the efficiency curve changes when this term goes to zero. As can be seen in Figure 3, the Q_{AUX} for ceria starts at zero due to the high value of the Q_{IC} heat benefit relative to the other terms in Q_{AUX} . When this Q_{IC} benefit value decreases significantly, Q_{AUX} becomes >0 , leading to the slope change at a $\Delta T \approx 25$ K. However, the Q_{H2O} term continues to decrease as the difference between the reduction and oxidation temperatures (ΔT) increases, leading to Q_{AUX} going to zero again. This yields the slope change at the η_{STH} maximum. By contrast, the ferrite/zirconia composite has a Q_{AUX} term that starts much higher and does not approach zero until higher values of ΔT . This is due to a number of reasons, including the fact that the Q_{H2O} term is much larger than the other terms in Q_{AUX} for the ferrite/zirconia composite. It should also be noted that

the magnitudes of Q_{AUX} and associated terms are much smaller for ferrite/zirconia than for ceria; this is why the η_{STH} for the ferrite/zirconia composite is so much larger than ceria.

In Figure 3, that the solids cooling heat benefit (Q_{SC}) is much larger for ceria than for ferrite/zirconia, despite the fact that the heat capacity for ferrite/zirconia ($187.9 \text{ J mol}^{-1} \text{ K}^{-1}$) is much higher than ceria ($80 \text{ J mol}^{-1} \text{ K}^{-1}$). This occurs because the normalized solids flow rate ($1/\Delta\delta$) for the ferrite/zirconia is much smaller than for ceria (see Figure 4). Because a smaller solids flow rate is needed, the solids cooling benefit (and the solids heating requirement) is correspondingly smaller for ferrites than for ceria.

Figure 4: Values for $\Delta\delta$ for ceria and ferrite/zirconia at a reduction temperature of 1,600 K and a reduction pressure of 0.1 Pa.

3.2. Illustration of Kinetics

The kinetic effects of oxidation on the overall STH efficiencies are taken into account by discounting the total efficiency values by the oxidation reaction rate for ceria and ferrite/zirconia as outlined in Section 2.1.9. These results are shown in Figure 5, and show that the impact of oxidation kinetics on ceria is minimal but significant for ferrite/zirconia. Even for the largest value of ΔT considered here (250 K), which correspond to low values of oxidation temperature, the overall impact on ceria efficiency is $<1\%$. This is not a trivial efficiency loss, but for the vast majority of ΔT values likely to be used, the oxidation kinetics have little noticeable impact on

ceria efficiency. However, for ferrite/zirconia the impact is large. At high values of ΔT , the kinetics effect on efficiency is >50% of the thermodynamic efficiency value.

a)

b)

Figure 5: Efficiency values with efficiency discounts for various values of ϵ_{GG} for a) ceria and b) ferrite/zirconia both with a reduction temperature of 1,600 K, a reduction pressure of 0.1 Pa, and a solid heat recuperation effectiveness of 50%.

Slow kinetics may be overcome by increased residence time or solid flowrates in the reactor, but this still has an impact on reactor performance and cost. Here, we attempt to quantify the effects of the oxidation kinetics on the thermodynamic efficiency to illustrate the impact of lower oxidation temperatures. While we are aware that an operating reactor would not lose productivity as simply as described, it does illustrate the general effects of different reaction rates on efficiency. An additional illustration of the time needed to overcome kinetic limitations at different oxidation temperatures is shown in Section S.8 of the Supplemental Material.

4. Discussion of Model Assumptions

Thermodynamic modeling is useful to illustrate trends and gain an understanding about trade-offs in a potential solar thermochemical system, even if the actual performance numbers will be different for a real system. Many previous analyses have examined the process impacts of ceria, though few studies have included a direct comparison of ceria with another active material. We will discuss the implications and tradeoffs within the system based on a new material. Then, the impact of material-specific oxidation kinetics for the two active materials, ceria and ferrite/zirconia, will be discussed.

4.1. Material Specific Effects on Thermodynamic Efficiency

Section 3.1 shows the thermodynamic efficiency of both ceria and a ferrite zirconia composite, which illustrates interactions between material-specific factors and the resulting impact on efficiency. By way of example, Scheffe *et al.* have suggested that a higher heat capacity active material may have a lower efficiency [45]. The results here show that the impact of sensibly heating the reactive solids for a material with a higher heat capacity might actually have a smaller impact on system efficiency if those same materials have a higher hydrogen productivity per mass of solids. Additionally, the results here illustrate the fact that different materials can have wildly different optimal operating conditions, and that these differences come from many different aspects of the process. There is no one parameter driving the optimal thermodynamic efficiency or set of optimal operating conditions; it is the result of a complex non-linear system that is difficult to predict *a priori*. This shows that this type of modeling is generally useful, especially for the impact of new assumptions and materials on the system.

Even though the efficiency values using the ferrite/zirconia composite are generally much higher than for ceria, this is not necessarily an endorsement or suggestion that this material is an ideal candidate for solar thermochemical water splitting. There is no experimental validation of the thermodynamic predictions of this material done here, and thus no sort of justification that this material could actually perform as described. Additionally, this material may suffer from kinetic limitations; this is described more below. Furthermore, it should be stated clearly that the authors do not necessarily consider either of these materials to be ideal candidates for STWS in an optimal process. These materials were used due to the availability of thermodynamic and kinetic information. There are many novel materials which may provide much better performance [46-49] but for which little or no thermodynamic and kinetic data are available for a variety of operational conditions. As with all thermodynamic models of this type, this comparison is still useful to illustrate trends and identify specific tradeoffs within the system.

4.2. Impact of Reaction Rates on Process Design

Section 3.1 illustrates the impact of kinetics on efficiency. Only the oxidation reaction rates are considered, not the reduction kinetics. The analysis assumes that the same reaction time will be used for all oxidation temperatures, when in a well-designed system the space-time would increase for the oxidation reactor to overcome these affects (albeit at some cost). However, this analysis illustrates the impact of reaction rates on process design when selecting the optimal operating conditions. Thermodynamic equilibrium is used both here and in other works to estimate material productivity and cycle efficiency, and these calculations can predict fairly large temperature swings between reduction and oxidation. The current attempt to include kinetics does quantify the drastic effect that reaction rates can have. Near-isothermal behavior thus becomes more optimal for materials with slower kinetics, and especially with moderate to high gas heat recuperation. The difference in ΔT_{opt} for thermodynamic equilibrium vs those calculated with the kinetic discounting is drastic for the ferrite/zirconia. Additionally, this analysis may be optimistic for ceria, as others have found ceria oxidation to be kinetically limited in some conditions [26]. Furthermore, this analysis points to the benefits of a flexible reactor design which can accommodate different conditions for reduction and oxidation as well as different flow rates between the two reaction zones. This would allow for reaction rates to be addressed in each reaction zone independently rather than running one or both reactions to less conversion.

5. Conclusions

A thermodynamic model has been developed for investigating various aspects of a solar thermochemical water splitting process. This model builds upon previous models described in the literature, and has expanded upon the prior state of the art by including a new material and kinetic effects. It uses a thermodynamic cycle of solid reactive material flowing between reduction and oxidation chambers. The model calculates flow rates, energy requirements, and energy benefits to produce one mole of hydrogen and uses these values to calculate the solar flux required to generate that amount of heat. The solar-to-hydrogen efficiency is then calculated for a variety of conditions and for two different materials.

In general, the ferrite/zirconia composite considered here displayed higher thermodynamic efficiency values than ceria, primarily due to the increased hydrogen production capacity of the material. Oxidation kinetics were also considered. Generally, the kinetic limitations to ceria are minimal except at very high ΔT values. The kinetic limitations for ferrite/zirconia are larger, causing large decreases in efficiency at even moderate ΔT values. This means that even for conditions that appear to be optimal for a particular material when considering only thermodynamic end-points, a very different set of operating conditions may be more efficient when kinetics are considered.

Acknowledgements

The authors would like to thank Dr. Ivan Ermanoski of Sandia National Laboratories for helpful discussion and comments about many aspects of the efficiency calculations. The authors would also like to thank Dr. Janna Martinek of the National Renewable Energy Laboratory for a helpful discussion about solar receiver losses. The authors are grateful for financial support from grant DE-EE0006671 from the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (EERE) and the Saudi Basic Industries Corporation (SABIC). BDE and CLM gratefully acknowledge financial support from Award P200A120125 of the U.S. Department of Education Graduate Assistance in Areas of National Need (GAANN) Program.

References

1. Winter, C.-J., *Hydrogen energy — Abundant, efficient, clean: A debate over the energy-system-of-change*. International Journal of Hydrogen Energy, 2009. **34**(14, Supplement 1): p. S1-S52.

2. U.S. Energy Information Administration (EIA). *Few transportation fuels surpass the energy densities of gasoline and diesel*. Today in Energy 2013; Available from: <http://www.eia.gov/todayinenergy/detail.cfm?id=9991>.
3. Ball, M. and M. Weeda, *The hydrogen economy – Vision or reality?* International Journal of Hydrogen Energy, 2015. **40**(25): p. 7903-7919.
4. *The Impact of Increased Use of Hydrogen on Petroleum Consumption and Carbon Dioxide Emissions*. 2008, U.S. Energy Information Administration (EIA).
5. Romero, M. and A. Steinfeld, *Concentrating solar thermal power and thermochemical fuels*. Energy & Environmental Science, 2012. **5**(11): p. 9234-9245.
6. Herron, J.A., et al., *A general framework for the assessment of solar fuel technologies*. Energy & Environmental Science, 2015. **8**(1): p. 126-157.
7. Alioshin, Y., et al., *High Temperature Electrolysis of CO₂ for Fuel Production*. Journal of The Electrochemical Society, 2016. **163**(2): p. F79-F87.
8. Siegel, N.P., et al., *Factors Affecting the Efficiency of Solar Driven Metal Oxide Thermochemical Cycles*. Industrial & Engineering Chemistry Research, 2013. **52**(9): p. 3276-3286.
9. Mallapragada, D.S. and R. Agrawal, *Limiting and achievable efficiencies for solar thermal hydrogen production*. International Journal of Hydrogen Energy, 2014. **39**(1): p. 62-75.
10. Koepf, E., W. Villasmil, and A. Meier, *Pilot-scale solar reactor operation and characterization for fuel production via the Zn/ZnO thermochemical cycle*. Applied Energy, 2016. **165**: p. 1004-1023.
11. Muhich, C.L., et al., *A review and perspective of efficient hydrogen generation via solar thermal water splitting*. Wiley Interdisciplinary Reviews: Energy and Environment, 2015.
12. Lange, M., et al., *T–S diagram efficiency analysis of two-step thermochemical cycles for solar water splitting under various process conditions*. Energy, 2014. **67**(0): p. 298-308.
13. Lange, M., et al., *Entropy Analysis of Solar Two-Step Thermochemical Cycles for Water and Carbon Dioxide Splitting*. Entropy, 2016. **18**(1): p. 24.
14. Bader, R., et al., *Thermodynamic Analysis of Isothermal Redox Cycling of Ceria for Solar Fuel Production*. Energy & Fuels, 2013. **27**(9): p. 5533-5544.
15. Krenzke, P.T. and J.H. Davidson, *On the Efficiency of Solar H₂ and CO Production via the Thermochemical Cerium Oxide Redox Cycle: The Option of Inert-Swept Reduction*. Energy & Fuels, 2015. **29**(2): p. 1045-1054.
16. Lapp, J., J.H. Davidson, and W. Lipiński, *Efficiency of two-step solar thermochemical non-stoichiometric redox cycles with heat recovery*. Energy, 2012. **37**(1): p. 591-600.
17. Bulfin, B., et al., *Thermodynamics of CeO₂ Thermochemical Fuel Production*. Energy & Fuels, 2015. **29**(2): p. 1001-1009.
18. Diver, R.B., et al., *Solar Thermochemical Water-Splitting Ferrite-Cycle Heat Engines*. Journal of Solar Energy Engineering, 2008. **130**(4): p. 041001-041001.
19. Singh, A.K., et al., *Thermal reduction of iron oxide under reduced pressure and implications on thermal conversion efficiency for solar thermochemical fuel production*. Industrial & Engineering Chemistry Research, 2015.
20. Furler, P., et al., *Thermochemical CO₂ splitting via redox cycling of ceria reticulated foam structures with dual-scale porosities*. Physical Chemistry Chemical Physics, 2014. **16**(22): p. 10503-10511.
21. Venstrom, L.J., et al., *Efficient Splitting of CO₂ in an Isothermal Redox Cycle Based on Ceria*. Energy & Fuels, 2014. **28**(4): p. 2732-2742.
22. Keene, D.J., J.H. Davidson, and W. Lipiński, *A Model of Transient Heat and Mass Transfer in a Heterogeneous Medium of Ceria Undergoing Nonstoichiometric Reduction*. Journal of Heat Transfer, 2013. **135**(5): p. 052701-052701.

23. Yuan, C., et al., *A new solar fuels reactor concept based on a liquid metal heat transfer fluid: Reactor design and efficiency estimation*. Solar Energy, 2015. **122**: p. 547-561.
24. Lange, M., et al., *Efficiency assessment of a two-step thermochemical water-splitting process based on a dynamic process model*. International Journal of Hydrogen Energy, 2015. **40**(36): p. 12108-12119.
25. Levêque, G. and S. Abanades, *Investigation of thermal and carbothermal reduction of volatile oxides (ZnO, SnO₂, GeO₂, and MgO) via solar-driven vacuum thermogravimetry for thermochemical production of solar fuels*. Thermochemica Acta, 2015. **605**(0): p. 86-94.
26. Venstrom, L.J., et al., *Applicability of an Equilibrium Model To Predict the Conversion of CO₂ to CO via the Reduction and Oxidation of a Fixed Bed of Cerium Dioxide*. Energy & Fuels, 2015. **29**(12): p. 8168-8177.
27. Xu, R. and T.F. Wiesner, *Conceptual design of a two-step solar hydrogen thermochemical cycle with thermal storage in a reaction intermediate*. International Journal of Hydrogen Energy, 2014. **39**(24): p. 12457-12471.
28. Muhich, C.L., et al., *A review and perspective of efficient hydrogen generation via solar thermal water splitting*. Wiley Interdisciplinary Reviews: Energy and Environment, 2016. **5**(3): p. 261-287.
29. Ermanoski, I., N.P. Siegel, and E.B. Stechel, *A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production*. Journal of Solar Energy Engineering, 2013. **135**(3): p. 031002-031002.
30. Panlener, R.J., R.N. Blumenthal, and J.E. Garnier, *A Thermodynamic Study of Nonstoichiometric Cerium Dioxide*. Journal of Physics and Chemistry of Solids, 1975. **36**: p. 1213-1222.
31. Bale, C.W., et al., *FactSage thermochemical software and databases — recent developments*. Calphad, 2009. **33**(2): p. 295-311.
32. *Hydrogen Analysis Resource Center: Lower and Higher Heating Values of Hydrogen and Fuels*. Available from: <http://hydrogen.pnl.gov/hydrogen-data/lower-and-higher-heating-values-hydrogen-and-other-fuels>.
33. Falcone, P.K., *Handbook for solar central receiver design*. 1986, Sandia National Laboratories: Livermore, CA.
34. Ermanoski, I., J.E. Miller, and M.D. Allendorf, *Efficiency maximization in solar-thermochemical fuel production: challenging the concept of isothermal water splitting*. Physical Chemistry Chemical Physics, 2014. **16**(18): p. 8418-8427.
35. Ehrhart, B.D. and D.D. Gill, *Evaluation of Annual Efficiencies of High Temperature Central Receiver Concentrated Solar Power Plants With Thermal Energy Storage*. 2013, Sandia National Laboratories: Albuquerque, NM.
36. Bulfin, B., et al., *Analytical Model of CeO₂ Oxidation and Reduction*. The Journal of Physical Chemistry C, 2013. **117**(46): p. 24129-24137.
37. Domalski, E.S. and E.D. Hearing, *Condensed Phase Heat Capacity Data*, in *NIST Chemistry WebBook, Standard Reference Database Number 69*, P.J. Linstrom and W.G. Mallard, Editors., National Institute of Standards and Technology: Gaithersburg, MD.
38. Ehrhart, B.D., et al., *System efficiency for two-step metal oxide solar thermochemical hydrogen production, Part 3: various methods for achieving low oxygen partial pressures in the reduction reaction*. International Journal of Hydrogen Energy, 2016. **Under Review**.
39. Sander, R., *Henry's Law Constants*, in *NIST Chemistry WebBook, Standard Reference Database Number 69*, P.J. Linstrom and W.G. Mallard, Editors., National Institute of Standards and Technology: Gaithersburg, MD.
40. Ehrhart, B.D., et al., *System efficiency for two-step metal oxide solar thermochemical hydrogen production, Part 2: impact of gas heat recuperation and separation temperatures*. International Journal of Hydrogen Energy, 2016. **Under Review**.

41. Arifin, D., *Study of redox reactions to split water and carbon dioxide*, in *Chemical and Biological Engineering*. 2013, University of Colorado: Boulder.
42. Scheffe, J.R., et al., *Kinetics and mechanism of solar-thermochemical H₂ production by oxidation of a cobalt ferrite-zirconia composite*. *Energy & Environmental Science*, 2013. **6**(3): p. 963-973.
43. Chueh, W.C. and S.M. Haile, *A thermochemical study of ceria: exploiting an old material for new modes of energy conversion and CO₂ mitigation*. *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences*, 2010. **368**(1923): p. 3269-94.
44. Scheffe, J.R. and A. Steinfeld, *Thermodynamic Analysis of Cerium-Based Oxides for Solar Thermochemical Fuel Production*. *Energy & Fuels*, 2012. **26**(3): p. 1928-1936.
45. Scheffe, J.R., D. Weibel, and A. Steinfeld, *Lanthanum–Strontium–Manganese Perovskites as Redox Materials for Solar Thermochemical Splitting of H₂O and CO₂*. *Energy & Fuels*, 2013. **27**(8): p. 4250-4257.
46. McDaniel, A.H., et al., *Sr- and Mn-doped LaAlO_{3-δ} for solar thermochemical H₂ and CO production*. *Energy & Environmental Science*, 2013. **6**: p. 2424-2428.
47. Takacs, M., J.R. Scheffe, and A. Steinfeld, *Oxygen nonstoichiometry and thermodynamic characterization of Zr doped ceria in the 1573-1773 K temperature range*. *Physical Chemistry Chemical Physics*, 2015. **17**(12): p. 7813-7822.
48. Al-Shankiti, I., et al., *Solar Thermal Hydrogen Production from Water over Modified CeO₂ Materials*. *Topics in Catalysis*, 2013. **56**(12): p. 1129-1138.
49. Rao, C.N.R., et al., *Solar photochemical and thermochemical splitting of water*. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 2016. **374**(2061).