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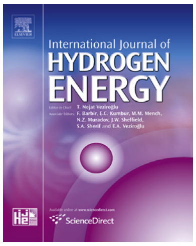

System efficiency for two-step metal oxide solar thermochemical hydrogen production – Part 3: Various methods for achieving low oxygen partial pressures in the reduction reaction

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ABSTRACT

The solar-to-hydrogen (STH) efficiency is calculated for various operating conditions for a two-step metal oxide solar thermochemical hydrogen production redox cycle to compare the effects of three methods for achieving low oxygen partial pressures for reduction. The calculations examine the effect on system efficiency of vacuum pump efficiency and inert gas/oxygen separation efficiency for a variety of reduction partial pressures using ceria as the active metal oxide. Currently available vacuum pump technologies have very low efficiencies at low pressures, and are unlikely to provide efficient hydrogen production relative to other oxygen partial pressure lowering technologies. Using currently available pumps arranged in a cascade pressure reduction configuration increases the effective pump efficiency significantly, but by less than an order of magnitude and, therefore, still results in low STH efficiencies for the system. If vacuum pumps could operate at a low pressure with an efficiency of ~10% or better, vacuum pumping (including cascade pressure reduction) has the potential to operate very efficiently for solar thermochemical hydrogen production. A novel recycled inert gas sweep with high temperature separation is suggested, and STH efficiency values vary significantly depending on the inert gas flowrate required, and will be reactor and reaction rate dependent. However, the use of an inert gas is likely able to take advantage of greater extents of reduction at very low oxygen partial pressures and produce high STH values if the inert gas/oxygen separation is ~10% efficient.

Introduction

Hydrogen has a number of important industrial uses and solar thermochemical water splitting is a way to produce renewable, carbon-free H_2 efficiently [1–4]. In two-step solar thermochemical reaction cycles, concentrated solar thermal energy provides the high temperatures necessary to reduce an active metal oxide material to produce oxygen. Steam is then passed over the reduced oxide to re-oxidize it, generating the

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Nomenclature

Greek letters

δ	extent of non-stoichiometry
η	thermal efficiency

Non-Greek letters

C_P	heat capacity, J mol^{-1} K^{-1}
N_C	number of chambers for cascade
$\dot{n}$	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 H_2, J/mol

Sub-scripts

amb	ambient
AR	after reduction
AUX	auxiliary
GG	gas–gas
H_2	property relating to hydrogen
H_2O	property or thermal energy relating to water
HOX	enthalpy of oxidation
HTR	enthalpy of reduction
i	index of cascade pressure reduction chamber
IC	inert cooling
IH	inert heating
io	ratio of inert to oxygen
MECH	mechanical
mix	mixing
MOL	energy related to producing 1 mol of H_2
O_2	property or thermal energy relating to oxygen
OX	oxidation
PUMP	property or thermal energy of pump work
RED	reduction
S	reactive solids
SC	solids cooling
SEP	property or thermal energy of separation
SH	solids heating
SOLAR	solar thermal energy
STH	solar-to-hydrogen
TC	thermal energy available for reaction

Super-scripts

‘	dummy variable for integration
eff	effective property
i	index of cascade pressure reduction chamber
N_2	property or thermal energy relating to nitrogen
REJ	Rejected heat

desired hydrogen product and reforming the original oxide material. The removal of oxygen from the reduction zone is critical for efficient hydrogen production in two-step metal oxide solar thermochemical redox cycles. In general, two methods have been suggested for removing the oxygen: vacuum pumping and an inert gas sweep [5,6]. Both of these methods physically transport the oxygen and lower the oxygen partial pressure in order to increase the extent of reduction of the active redox material.

Some studies have suggested that in a process at scale, vacuum reduction leads to higher efficiencies than using an inert gas sweep [7,8]. However, this type of large scale vacuum process is difficult to implement. Ermanoski [9] showed that a single vacuum pump is unlikely to achieve large scale O_2 removal at the low pressures required for solar thermal water splitting due to the huge volumetric flowrates and associated gas velocities; therefore, a cascade pressure reduction system was suggested. In such a system, several chambers are used in which a pump pulls a vacuum on each individual chamber and each chamber has a sequentially lower pressure. Brendelberger and Sattler consider cascade systems with one, two, and three chambers, and found that while the system efficiency increase was significant, it suffered from diminishing returns even on the third chamber, and that the total system efficiency increase was <5% [10]. Additionally, others have suggested that previous analyses over-estimate the efficiency at which vacuum pumps operate, leading to a significant change in pump work required [11,12].

Recent studies have also examined the possibility of highly efficient inert gas sweeping. Several gas flow configurations and production methods have been proposed. Some prior works [7,11] only considered a mixed gas system instead of a counter-flow arrangement, and the much higher inert gas flowrates calculated in this way tend to show that vacuum reduction is more efficient, even with limited pump efficiency values [11]. Other works compared counter-flow to perfect mixing [13] and parallel-flow [14,15] arrangements, and showed that the counter-flow was more efficient, but suggested that the final flow arrangement would be an intermediate state. Brendelberger et al. [16] examined limitations on the counter-flow arrangements and developed models to approximate this middle ground. Past work has suggested producing N_2 continuously from surrounding air, but the energy requirements are very high [7]. Others have suggested recycling inert gas, rather than producing it in an open-loop fashion [14,17]. Still others have suggested using both an inert sweep gas and vacuum pumping simultaneously, and have compared the energy required for inert gas and vacuum [13,18].

In this work, we use a thermodynamic model [4] to explore the effect of O_2 removal methods on the overall solar-to-hydrogen (STH) efficiency. Specifically, we expand on previous studies that consider the vacuum pump efficiency by considering a wide range of vacuum pump efficiency values, including but not limited to currently available pump technologies. We also quantify the impact of cascade pressure reduction on STH efficiencies. Lastly, we propose the use of a recycled inert sweep gas with a high temperature purification step and illustrate its impact on system efficiency, along with a direct comparison of all of these possibilities.

Methods

To determine the STH efficiency of the system, we employ a numerical model which was developed in Ref [4] and uses ceria as an example material. Here we will describe key parts of the model and highlight changes to equations within the model.

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