Title:

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 design pressures using ceria as the active metal oxide. Currently available vacuum pump technologies have very low thermodynamic 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.

Nomenclature

Greek Letters

δ	Extent of non-stoichiometry
η	Thermal efficiency

Non-Greek Letters

C_P	Heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)
N_C	Number of chambers for cascade pressure reduction
$\dot{n}$	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)

Sub-Scripts

amb	Ambient
AR	After reduction
AUX	Auxiliary
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
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 one mole of hydrogen

O2	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 thermochemical reaction

Super-Scripts

‘	A dummy variable for integration
eff	Effective property
i	Index of cascade pressure reduction chamber
N2	Property or thermal energy relating to nitrogen

1. 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 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 [5-7]. Both of these methods physically transport the oxygen and lower the oxygen partial pressure to below ambient 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 [8, 9]. However, this type of large scale vacuum process is difficult to implement. Ermanoski [10] 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 the 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% [11]. Additionally, others have suggested that previous analyses over-estimate the efficiency at which vacuum pumps operate, leading to a drastic increase in pump work required [12, 13].

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 [8, 12] 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 [12]. Other works compared counter-flow to perfect mixing [14] and parallel-flow [15, 16] 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.* [17] examined limitations on the counter-flow arrangements and developed models to approximate this middle ground. Past work has suggested producing nitrogen continuously from surrounding air, but the energy requirements for this method of operation are very high [8]. Others have suggested recycling inert gas, rather than producing it in an open-loop fashion [15, 18]. Still others have suggested using both an inert sweep gas and vacuum pumping simultaneously [14]. In addition to the direct study of inter gas sweeping, other works have compared the energy required for inert gas and vacuum [14, 19].

In this work, we use a thermodynamic model [4] to explore the effect of O₂ 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.

2. Methods

To determine the STH efficiency of the system, we employ a numerical model which was developed in a 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.

2.1. Efficiency Calculations for Thermodynamic Equilibrium

A thermodynamic model is used to calculate mass and energy flows through a solar thermochemical system. The details of this model are described elsewhere [4], but the overall efficiency equations will be briefly described again here. Then, energy requirements for the three different methods of attaining low oxygen partial pressure will be detailed. It is important to note that the energy flows in this model are normalized to one mole of hydrogen produced.

2.1.1. Overall System Description

We consider an overall process, as shown in Figure 1, in which concentrated solar radiation is used to drive a two-step metal oxide thermal reduction and oxidation reaction cycle. It should be noted that this model is a simplified and idealized model of a potential system that is meant to be as general as possible. There are many tradeoffs that result from various design choices that are

not discussed or included here. This model is meant to show what is theoretically possible to achieve, not how a real system would behave. A significant difference between this work and previously used models [4] is that the model uses both vacuum reduction and an inert gas sweep. This will be discussed in more detail below.

Figure 1: Model process schematic, not to scale. Line arrows indicate mass flows, while block arrows indicate energy flows. A block arrow directed into a block is a heat requirement, a block arrow directed out of a block is a heat benefit. A filled block arrow denotes an energy flux per unit time, and empty block arrow denotes an energy requirement per mole of hydrogen. The empty block arrows sum to equal the $\dot{Q}_{MOL}$ term.

We define the system efficiency (η_{STH}) as the chemical energy in hydrogen (using the higher heating value, HHV) divided by the amount of earth-incident solar energy required to produce that hydrogen by the proposed process ($\dot{Q}_{SOLAR}$), as shown in Equation (1).

$$\eta_{STH} = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_{SOLAR}} \quad (1)$$

The system models the energy required to produce a single mole of hydrogen (Q_{MOL}), and this is determined by the thermal reduction endotherm of the solid material (Q_{HTR}), the sensible energy needed to heat the reactive solids to the reduction temperature (Q_{SH}), the energy required to heat the inert gas up to the reduction temperature (Q_{IH}), and other auxiliary heating requirements (Q_{AUX}), as shown in Equation (2).

$$Q_{MOL} = Q_{HTR} + Q_{SH} + Q_{IH} + Q_{AUX} \quad (2)$$

The auxiliary heating requirement (Q_{AUX}) includes heat requirements that occur primarily at or below the oxidation temperature. These terms include water heating requirements (Q_{H_2O}), pump work (Q_{PUMP}), mechanical work (Q_{MECH}), separations work (Q_{SEP}). Q_{AUX} also includes heat benefits to the system, including the exothermic enthalpy change from the oxidation reaction (Q_{HOX}), the un-recuperated heat in the solid flow as it cools (Q_{SC}), the un-recuperated heat of the inert gas as it cools (Q_{IC}), and the heat from cooling the oxygen stream (Q_{O_2}). The overall auxiliary heating equation is calculated by Equation (3).

$$Q_{AUX} = (Q_{H_2O} + Q_{PUMP} + Q_{MECH} + Q_{SEP}) - (Q_{HOX} + Q_{SC} + Q_{IC} + Q_{O_2}) \quad (3)$$

2.1.2. Vacuum Pump Case

Vacuum pump work (shown in Equation (4)) incorporates the heat-equivalent of the work necessary for pumping oxygen. This was assumed to be zero in a previous analysis which considered only inert sweeping [4], but is considered here because of the changing reduction pressure. The heat equivalent is calculated for pumping one half mole of oxygen from the reduction pressure (p_{RED}) to ambient pressure ($P_{amb} = 1 \text{ atm} = 101,325 \text{ Pa}$). This is done at ambient temperature (T_{amb}). Here, the reduction oxygen partial pressure (p_{RED}) is equal to the total pressure of the reduction zone (P_{RED}). An efficiency factor (η_{PUMP}) is used to convert from pump work to heat equivalent. This factor is calculated based on the reduction pressure being considered, and an interpolation of the pump efficiency data from Bulfin *et al.* [12]. Details of this calculation, as well as a plot showing the pump efficiency η_{PUMP} used is shown in Section S.1 of the Supplemental material. If inert gas is to be used (as described below in Section 2.1.4), then the pump work (Q_{PUMP}) is set to zero.

$$Q_{PUMP} = \frac{n_{O_2} RT_{amb}}{\eta_{PUMP}} \ln \left(\frac{P_{amb}}{p_{RED}} \right) \quad (4)$$

Since pump work involves a conversion from pump work to heat equivalent, there is some amount of heat rejected in that conversion. This rejected heat for the pump work (Q_{PUMP}^{REJ}) is calculated in Equation (5), and contributes to the total rejected heat per mole of hydrogen (Q_{REJ}^{MOL}).

$$Q_{PUMP}^{REJ} = (1 - \eta_{PUMP}) Q_{PUMP} \quad (5)$$

2.1.3. Cascade Pressure Reduction Case

In addition to the single-pump work term shown above, we also consider a cascade pressure reduction method. In cascade pressure reduction, each pump is assumed to have an identical volumetric flow rate. A schematic of this type of cascade pumping is shown in Figure 2.

Figure 2: A schematic (not to scale) of a cascade pressure reduction system for N_C chambers. Each pressure reduction chamber has an equally sized vacuum pump attached to it, which pumps an equal volumetric flow rate of oxygen at an efficiency based on the pressure of that stage of the cascade. The molar flow rate of oxygen for each chamber is based on the temperature and pressure of that chamber. It is assumed the reactive solids reach thermodynamic equilibrium in each chamber. Chamber 0 is a chamber with no pump for when the equilibrium partial pressure of oxygen is >1 atm.

An effective pump efficiency of the system is calculated by dividing the work required to pump the oxygen in a single, perfectly efficient pump by the total work required by the cascade pump series. This is done in order to directly compare pump efficiency values for this and the above single-pump systems. The final expression is shown in Equation (6). Here, η_{PUMP}^{eff} is the effective pump efficiency, $\dot{n}_{O_2}$ is the total molar flow rate of oxygen per unit time, P_{amb} is the ambient pressure, p_{RED} is the final reduction pressure, N_C is the number of chambers considered, $\dot{n}_{O_2}^i$ is the molar flow rate per unit time of oxygen from the i^{th} chamber, η_{PUMP}^i is the pump efficiency at the pressure of the i^{th} chamber, and p_i is the pressure of the i^{th} chamber. The cascade pump system and the sizes (volumetric flow rates) of the pumps are solved iteratively, using equations from Ermanoski [10]. After the effective pumping efficiency is calculated, the pump work (Q_{PUMP}) is calculated using Equation (4). Details on how this effective pump efficiency was calculated are given in Section S.2 of the Supplemental Material.

$$\eta_{PUMP}^{eff} = \dot{n}_{O_2} \ln \left(\frac{P_{amb}}{p_{red}} \right) \left[\sum_{i=1}^{N_C} \frac{\dot{n}_{O_2}^i}{\eta_{PUMP}^i} \ln \left(\frac{P_{amb}}{p_i} \right) \right]^{-1} \quad (6)$$

Additionally, the effective pump efficiency for cascade pressure reduction is also considered for the limiting case of an infinite number of reduction chambers. The resulting equation is shown in Equation (7), and this is consistent with an independently derived expression for the upper limit of vacuum pump efficiency [13]. Here, $\dot{n}_S$ is the solids flow rate per unit time, δ_{RED} is the extent of non-stoichiometry of the fully reduced material, and δ_0 is the extent of non-stoichiometry of the material as it enters the infinite cascade pressure reduction system. Additional details are available in Section S.2 of the Supplemental Material.

$$\eta_{PUMP}^{eff,inf} = \frac{2\dot{n}_{O_2}}{\dot{n}_S} \ln \left(\frac{P_{amb}}{p_{RED}} \right) \left[\int_{\delta_0}^{\delta_{RED}} \frac{\ln \left(\frac{P_{amb}}{p_i(\delta')} \right)}{\eta_{PUMP}^i(\delta')} d\delta' \right]^{-1} \quad (7)$$

2.1.4. Inert Gas Sweep Case

The inert sweep gas is assumed to be N_2 operating in a counter-flow inert gas/solids arrangement, and that each infinitesimal point along the solid/gas contact reaches local thermodynamic equilibrium. A schematic of this (showing the reduction zone and inert gas loop only) is shown in Figure 3.

Figure 3: Flow diagram schematic (not to scale) for reduction using an inert gas. The rest of the process (oxidation, etc.) is not shown.

The required amount of inert gas is calculated as a ratio of moles of inert gas per mole of oxygen (n_{io}); this calculation is similar to previous studies [15, 18] and is shown in Equation (8). 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. p_{AR} is obtained by calculating the equilibrium oxygen partial pressure above the reactive solids that is at the reduction temperature (T_{RED}) and the oxidized stoichiometric state (δ_{OX}). This amount of inert gas is only the minimum amount required to achieve a level of dilution of the O_2 in the final stream. Results in this work only consider this minimum flowrate, but a separate analysis considers the impact of changing this flowrate [20].

$$n_{io} = \left(\frac{p_{AR}}{P_{RED} - p_{AR}} - \frac{p_{RED}}{P_{RED} - p_{RED}} \right)^{-1} \quad (8)$$

Equation (9) shows the separation work for inert/ O_2 separation, where $T_{SEP}^{O_2}$ is the oxygen/inert gas separation temperature, $\eta_{SEP}^{O_2}$ is the oxygen/inert separation efficiency (assumed to be 15%), and ΔS_{mix} is the entropy of mixing of each sub-stream (the explicit equation for ΔS_{mix} is given in Ref [4]). The mole fractions are calculated using the oxygen partial pressures that were used to calculate n_{io} (Equation (9)). An oxygen product purity after separation of 100% was assumed because of the closed system, and the oxygen partial pressure

for reduction (p_{RED}) was used to determine the final effluent oxygen concentration. The $T_{SEP}^{O_2}$ is assumed to be 1,223 K (950 °C); this is consistent with a high temperature ion transport membrane [21], and this temperature is more fully considered in a separate analysis [20]. Since separation work includes a conversion to heat equivalent, the rejected heat from this conversion ($Q_{SEPO_2}^{REJ}$) is given in Equation (10).

$$Q_{SEP}^{O_2} = \frac{T_{SEP}^{O_2}}{\eta_{SEP}^{O_2}} (\Delta S_{mix}^{product} + \Delta S_{mix}^{effluent} - \Delta S_{mix}^{feed}) \quad (9)$$

$$Q_{SEPO_2}^{REJ} = (1 - \eta_{SEP}^{O_2}) Q_{SEP}^{O_2} \quad (10)$$

2.2. Calculation Method and Parameters

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 reduction temperature (T_{RED}) of 1,800 K was considered. A variety of oxidation temperatures were considered, which are related to the temperature difference between reduction and oxidation ($\Delta T = T_{RED} - T_{OX}$). ΔT values of 0 - 800 K (step size of 10 K) were used. Ceria was used as the active material. Both the reduction and oxidation reactions are assumed to take place at 1 atmosphere (101,325 Pa). Solid heat recuperation can occur between the active material as it is heated and cooled as it cycles between the reduction and oxidation temperatures; the fraction of the amount of this heat that is recuperated in a useful way is described by the solid-solid heat recuperation effectiveness (ϵ_{SS}). Gas heat recuperation can occur between both the steam before and after it enters the oxidation reactor as well as the inert gas as it cycles between the reduction reactor and the separator. Similar to the solids, the fraction of this heat that is recovered is described by the gas-gas heat recuperation effectiveness (ϵ_{GG}). Values for ϵ_{SS} and ϵ_{GG} from 0-100% were included to illustrate bounds on the possible effects of these parameters. A more thorough description of all of these values and how they are incorporated into the model is given in Ref [4]. Additionally, two example calculations are given in Section S.3 of the Supplemental Information with operating conditions, constants, and all major calculated values.

3. Results

System efficiency values will be presented for three methods of achieving low oxygen partial pressures. Direct vacuum pumping will be considered first, followed by cascade pressure

reduction, and then an inert gas case will be presented. For each case, the sensitivity of critical assumptions on system efficiency will also be shown.

3.1. Efficiency of Vacuum Pumping

The STH efficiency is shown in Figure 4 for the complete range of gas heat recuperation values for O₂ removal by vacuum pumping at efficiencies of currently available pumps.

Figure 4: Solar to hydrogen thermal efficiency (η_{STH}) values for various ΔT values and various gas heat recuperation effective values (ϵ_{GG}). All of these values are calculated for ceria at a reduction temperature (T_{RED}) of 1,800 K, a reduction pressure (p_{RED}) of 10 Pa, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

The system efficiencies are quite low when the vacuum pump efficiency values of current pumps are considered. This is because pumping at low pressures thermodynamically requires exponentially more work (from the $\ln(P_{\text{amb}}/p_{\text{red}})$ term in Equation (4)) and pumping at low pressures has even lower theoretical-to-actual work efficiencies. The pump work dominates the Q_{AUX} and Q_{MOL} terms, which has a detrimental impact on system efficiency. Specific energy terms for these conditions showing this can be seen in Section S.4 of the Supplemental Information.

The pump efficiency is greatly affected by the reduction pressure, and so the impact of different reduction pressures on system efficiency is shown in Figure 5. The STH efficiency is very low at very low reduction pressures (< 10 Pa) due to both exponentially increasing pump

work (the $\ln(P_{\text{amb}}/p_{\text{red}})$ term in Equation (4)), and the exponentially decreasing pump efficiency (the η_{PUMP} term in Equation (4)). The STH efficiencies are also low at higher reduction pressures (10,000 Pa), in this case due to the substantially lower reduction extent of the material. A lower extent of reduction (smaller value of δ_{RED}) leads to a larger solids flowrate which increases sensible heating and mechanical work requirements, as well as a larger amount of excess steam required for oxidation, which leads to significantly higher sensible heating requirements. As such, the optimum reduction pressure for this type of system is somewhere near a more moderate (1,000 Pa) reduction pressure.

These analyses primarily consider the point at which the system efficiency (η_{STH}) reaches the highest point; the ΔT value at which this is reached is denoted ΔT_{opt} . For example, in Figure 5 the case for the 1,000 Pa reduction pressure has a lower system efficiency than the case for 100 Pa reduction pressure for ΔT values < 150 K. However, the $p_{\text{RED}} = 1,000$ Pa case reaches a maximum $\eta_{\text{STH}} \approx 0.12$ at $\Delta T_{\text{opt}} \approx 350$ K, whereas the $p_{\text{RED}} = 100$ Pa case only reaches $\eta_{\text{STH}} \approx 0.05$ at $\Delta T_{\text{opt}} = 800$ K. There are a number of reasons for the different shape of the various lines in Figure 5; the model describes a complex non-linear system, but a few major trends are worth identifying. First, some of the cases for the higher reduction pressures ($p_{\text{RED}} \geq 100$ Pa) show a discontinuity at low ΔT values; this is due to the fact that at such a high partial pressure of oxygen, the thermodynamic cycle is simply not feasible with such a small temperature swing, no matter how much water is used for oxidation. This is described in more detail in previous works [18, 22]. The other major trend is the fact that two of the η_{STH} lines in Figure 5 ($p_{\text{RED}} = 1,000$ and $p_{\text{RED}} = 10,000$ Pa) first increases, reaches a peak, and then decreases whereas other lines monotonically increase η_{STH} with increasing ΔT . This is due to the Q_{AUX} term reaching a zero value, and which is when the heat benefits outweigh the auxiliary heating requirements; this is described further in other works in this series [4, 22]. It should be noted that for these (and subsequent) analyses, the reduction pressures being considered are order-of-magnitude estimates, and are not optimized.

Figure 5: η_{STH} values for various ΔT values and various reduction pressures (p_{RED}). All of these values are calculated for ceria at a reduction temperature (T_{RED}) of 1,800 K, a gas heat recuperation effectiveness (ϵ_{GG}) of 0.9, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

In addition to comparing real pump data for vacuum reduction with other methods of reduction below, we also examined the effect of the pump efficiency itself. This is done not because of any preference to any specific pumping technology, but rather to see the full range of vacuum pump efficiency values and the impact that these will have on the overall STH efficiency. Singh *et al.* [9] have analyzed the effect of vacuum pump efficiencies before, but these results are included here both as a direct comparison to other results in this work, as well as the fact that these results show the effect of different vacuum pump efficiency values on the entire system, rather than just the reduction reaction terms. The results of these were done for the highest (10,000 Pa) and lowest (0.1 Pa) reduction pressures considered, and the results are shown in Figure 6.

a)

b)

Figure 6: η_{STH} values for various vacuum pump efficiency values for 1) $p_{RED} = 0.1$ Pa and b) $p_{RED} = 10,000$ Pa. All calculations were done for a reduction temperature of 1,800 K, a gas heat recuperation effectiveness of 0.9, and a solid heat recuperation effectiveness of 0.5.

Unsurprisingly, order-of-magnitude increases to vacuum pump efficiency at low efficiency values have the greatest positive impact on STH efficiencies, relative to the smaller increases at higher pump efficiency values. If vacuum pumps could operate at a low pressure with an efficiency of ~10% or better, vacuum pumping has the potential to facilitate highly efficient solar thermochemical hydrogen production. Efficiency gains above this level have more moderate impacts on system efficiency: the difference in optimum STH efficiency values between $\eta_{\text{PUMP}} = 0.1$ and $\eta_{\text{PUMP}} = 1.0$ is <5%. This is because after a critical level of pump efficiency, the vacuum pump work required becomes small relative to other heating requirements. For higher reduction pressures, these impacts are generally the same, but much more muted; for example, at $p_{\text{RED}} = 10,000$ Pa the only significant change in optimal η_{STH} values occurred between $\eta_{\text{pump}} = 0.001$ and 0.01. At η_{pump} values ≥ 0.01 , the η_{STH} values are relatively unchanged. This is because the thermodynamic pumping work for compressing the oxygen is less, meaning that the pump has less of an impact on the final value of the Q_{PUMP} term. The STH efficiency values are much lower ($\eta_{\text{STH}} < 10\%$) for the high pressure case because of the lower extent of reduction achieved.

3.2. Efficiency of Cascade Pressure Reduction

The STH efficiency results for a cascade pressure reduction system with five chambers using currently available pump efficiencies are shown in Figure 7 for a variety of gas heat recuperation values. As can be seen, the system efficiencies are still quite low. This is because effective pump efficiency value for five chambers is still very low (~0.00025%). Thus, the pump work dominates the other heat requirements for the rest of the system. This is shown explicitly in Section S.4 of the Supplemental Information.

Figure 7: System efficiency (η_{STH}) for a cascade pressure reduction system with 5 chambers. All of these values are calculated for ϵ_{SS} at a reduction temperature (T_{RED}) of 1,800 K, a reduction pressure (p_{RED}) of 1 Pa, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

The STH efficiency for various reduction pressures is shown in Figure 8. As can be seen, the same general trends are followed that were shown for a single vacuum chamber system (Figure 5). At very low pressures, the STH efficiency is low due to the very high amounts of pump work required. At very high pressures, the active material is not reduced enough to be operated efficiently. However, at a moderate pressure (~ 100 Pa), the system will reach an optimum. This exact value is somewhat different for a system with five chambers than it is for a system with one chamber, due to the change in effective pump efficiency. It should be noted, though, that the five chamber case has higher STH efficiency values than the single chamber case.

Figure 8: System efficiency (η_{STH}) for a cascade pressure reduction system with five chambers. All of these values are calculated for ceria at a reduction temperature (T_{RED}) of 1800 K, a gas heat recuperation effectiveness (ϵ_{GG}) of 0.9, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

Effective pump efficiencies for various numbers of chambers are shown in Figure 9(a). As can be seen, the effective pump efficiency increases moderately for systems with more chambers, but not necessarily by orders of magnitude. This is because different chambers are pumped at different pressures and thus at different efficiencies. However, even for the limiting case of a system with an infinite number of chambers, the effective pump efficiency is still relatively low (between 0.00025% and 0.00045%). This still very low effective vacuum pump efficiency at a low reduction pressure leads to still very low system efficiency values, which are shown in Figure 9(b).

a)

b)

Figure 9: a) effective pump efficiency ($\eta_{\text{PUMP}}^{\text{eff}}$) and b) solar to hydrogen efficiency (η_{STH}) values for cascade pressure reduction systems with various numbers of chambers. All the calculations here are done for ceria at a reduction temperature (T_{RED}) of 1,800 K and a final reduction pressure (p_{RED}) of 1 Pa.

Though the improvement at very low reduction pressures is not very high due to the still low effective vacuum pump efficiency values, Figure 8 shows that more moderate pressures have higher system efficiency values. Additionally, the same moderate pressures have the highest improvement to effective pump efficiency (shown in Section S.5 of the Supplemental Information). These two effects can therefore be combined to see the maximum system

improvement possible on the system efficiency (within the values considered here), and this is shown in Figure 10 for $p_{\text{RED}} = 100$ Pa. The largest increases in system efficiency occur for 2 and 5 cascade chambers, while additional chambers above this value have much less of an effect on the maximum η_{STH} . This reflects the improvement to the effective pump efficiency on the reduction pressure that is most sensitive to this change, as discussed above. Conversely, the system efficiency is almost entirely unchanged for higher reduction pressures due to the negligible impact that vacuum pump work has on system efficiency, even for an infinite number of cascade chambers (shown in Section S.5 of the Supplemental Information). All of the system efficiency values calculated for pressures and cascade configurations calculated are given in Section S.5 of the Supplemental Information for comparison.

a)

b)

Figure 10: a) effective pump efficiency ($\eta_{\text{PUMP}}^{\text{eff}}$) and b) solar to hydrogen efficiency (η_{STH}) values for cascade pressure reduction systems with various numbers of chambers. All the calculations here are done for ceria at a reduction temperature (T_{RED}) of 1,800 K and a final reduction pressure (p_{RED}) of 100 Pa.

3.3. Efficiency of Inert Sweep Gas Reduction

The system efficiency using inert gas reduction for various gas heat recuperation values is shown in Figure 11, and the specific heat requirements are shown Section S.4 of the Supplemental Information. The decreasing value of inert gas heating requirements (Q_{IH}) and inert gas/oxygen separation work ($Q_{\text{SEP}}^{\text{O}_2}$) with increasing ΔT are due to the decreasing inert gas flowrate (n_{iO}) required, and lead to the increasing η_{STH} at low values of ΔT . At higher values of ΔT (>200 K), the inert gas flowrate has decreased to zero, meaning that further increases to system efficiency from decreasing inert gas requirements are not possible; instead, the system efficiency decreases due to the increasing sensible heating of the reactive solids (Q_{SH}).

Figure 11: System efficiency (η_{STH}) for inert gas sweep system. All of these values are calculated for ceria at a reduction temperature (T_{RED}) of 1,800 K, a reduction pressure (p_{RED}) of 0.1 Pa, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

The use of an inert gas sweep is especially useful to achieve very low oxygen partial pressures, which in turn gives high STH efficiency values. The system efficiency tends to decrease at higher oxygen partial pressures for reduction. This is because as the solid achieves a greater extent of reduction, it is oxidized more easily. This means that less excess steam is required to oxidize the material, and less overall active redox material is needed to produce the same amount of hydrogen. As the reduction oxygen partial pressure increases, the inert gas requirements decrease, but the benefits from greater extents of reduction also decrease. This is shown in Figure 12.

Figure 12: System efficiency (η_{STH}) for inert gas sweep system with different reduction pressures. All of these values are calculated for ceria at a reduction temperature (T_{RED}) of 1,800 K, a reduction pressure (p_{RED}) of 0.1 Pa, a gas heat recuperation effectiveness (ϵ_{GG}) of 0.9, and a solid heat recuperation effectiveness (ϵ_{SS}) of 0.5.

The STH efficiency shown above depends greatly on the inert gas flowrate, as this impacts the inert gas sensible heating and cooling terms as well as the inert/oxygen separation work. As such, the inert gas flowrates calculated for the full range of reduction oxygen partial pressures considered are shown in Figure 13. The flowrates for the very low (≤ 10 Pa) oxygen partial pressures are similar, but the behavior changes for reduction partial pressures of 100 Pa and above. This is because at very low ΔT values, the reduction and oxygen reactions simply do not proceed because the reduced material is no longer able to split water. This is consistent with previous studies which have shown that ceria is unable to undergo a reduction/oxidation cycle at low ΔT values and high oxygen partial pressures [18, 22]. The exact ΔT value at which the cycle is thermodynamically viable requires an infinite inert gas flowrate because $\Delta\delta = 0$, meaning that there will be an infinite solids flowrate, an infinite oxygen flowrate, and thus an infinite inert gas flowrate. The n_{io} plots that include very large ($>1,600$) n_{io} values are truncated in Figure 13 for ease of viewing. The effect of non-minimum inert gas flowrates (such as those calculated here) are considered in a separate analysis [20].

Figure 13: Inert gas flowrate ratio (n_{io}) for use in an inert gas sweep for reduction at various reduction oxygen partial pressures. Calculations were done for ceria with a reduction temperature of 1,800 K.

The effect on overall STH efficiency for a wide range of inert/oxygen separation efficiency values (0.001 to 1.0) are shown in Figure 14. The result of a lower oxygen separation efficiency is lower STH efficiency at low ΔT values due to the increase of oxygen/inert separation work. STH efficiency values at higher ΔT values are similar, due to the fact that the inert gas flowrate goes to zero (which is not realistic). However, the results in Figure 14 do indicate that an oxygen/inert separation efficiency of ~10% will give very high STH efficiencies for this active material and set of conditions. This is because the optimal efficiency and ΔT value are not at the same point as the lower efficiency curves; that is, it is not when $n_{io} \approx 0$. Thus, this shows that if an efficiency value of ~10% can be achieved, the inert gas sweep option is likely to achieve the STH efficiencies necessary for commercialization of this process (for this set of conditions). Additionally, these results show that improving the inert/oxygen separation efficiency much above 10% will likely have little additional impact on overall STH efficiency. It should also be noted that separation efficiencies below 10% also give high STH efficiencies, but these high

STH efficiency values occur when n_{i0} is at or near zero. Thus, the actual STH efficiency values at lower inert/O₂ separation efficiencies will depend on the case-specific inert gas ratio used.

Figure 14: η_{STH} values for ceria at various inert/oxygen separation efficiency values. All calculations were done at a reduction temperature of 1,800 K, a reduction oxygen partial pressure of 0.1 Pa, a gas heat recuperation effectiveness of 0.9, and a solid heat recuperation effectiveness of 0.5.

4. Discussion of Model Assumptions

The practicality of achieving some of the assumptions used above will be discussed. Specifically, limitations on vacuum pump efficiency improvements will be discussed, both in the context of direct and cascade pressure reduction. Additionally, the critical assumptions for the recycled inert gas sweep will be discussed, including the flow rates and separation efficiency.

4.1. Feasibility of High Vacuum Pump Efficiency

It is difficult to determine what a realistic value for a vacuum pump efficiency will be. Two factors affect this, solar to electric efficiency and electric to pump work efficiency. As solar-to-electric efficiency values rise due to improvements with photovoltaics, concentrated solar thermal power cycles, or other methods, the overall solar-to-pump work efficiency will rise. However, even the most optimistic performance targets (which have not been demonstrated) for

concentrated solar power are for a solar-to-electric efficiency of 50% [23], not that much higher than the currently assumed value of 40%. As such, it is of more interest to consider possible improvements to the electric-to-work efficiency for vacuum pumps.

Current technologies for near-atmospheric compressors are between ~70-80% efficient [15, 24]. However, vacuum pumps face challenges because of the inherently low mass flows associated with vacuum pumping, which yield energy efficiencies of a single-digit percent or less [25]. This means that pump and compressor efficiency values that can be assumed from other technologies can not necessarily be applied to low pressures. That said, we know of no fundamental limit on vacuum pump efficiency for very low pressures. As such, we do not limit the possibility of higher vacuum pump efficiency values, and an increase to this value will certainly have an impact on STH efficiency; this is shown in Section 3.1 and reflected in many other works [12, 14, 17, 22]. It is likely that future advancements in vacuum pump technologies will increase vacuum pump efficiency values, possibly driven by economic market forces based on an increase in demand for high-efficiency, high-vacuum pumps. However, vacuum pumps have fewer physical gas molecules to pump, making them inherently less efficient at lower pressures. Thus, it is not likely that these increases will lead to improvements in vacuum pump efficiency of multiple orders of magnitude which would be necessary to match the efficiencies of efficient inert gas use.

4.2. Practicality of Cascade Pressure Reduction

Some type of multi-pump cascading pressure system may be helpful for any type of large-scale solar thermochemical hydrogen production system that uses vacuum-driven reduction. The large scale and low pressures give rise to enormous volumetric flow rates, which a single pump is unlikely to be able to handle. However, while the gains in effective pump efficiency using multiple cascading pumps are significant, they are less than a single order of magnitude, similar to the results of Brendelberger and Sattler [11]. Even for an infinite number of chambers, the increase in effective pump efficiency does not have a large impact on system efficiency for low reduction pressures; this is consistent with the findings by Jarrett *et al.* [13]. However, this increase in effective pump efficiency does change the optimum system efficiency and optimal operating conditions at higher reduction pressures, showing that this does have an effect on overall system efficiency for some conditions.

The current analysis assumed that each vacuum pump in the cascading system would have the same volumetric flowrate. This is not necessarily the most efficient way to operate, and other strategies were not explicitly explored here. However, we do not foresee a drastic change in effective pump efficiency based on changing the volumetric flowrate distribution. This is because increasing the flowrate of pumps in the beginning of the cascade (at higher pressures) so that they do more of the pump work at a higher pump efficiency will mean that the chambers for those pumps will operate at a lower pressure, thus negating the gain in pump efficiency.

Another aspect not considered here is the economic impact of additional vacuum pumps. Obviously, there are a minimum number of pumps required to achieve a certain pressure at a certain scale, because pumps can realistically only be so large. However, increasing the number of pumps beyond this minimum number will have significant economic impacts on any system. These economic impacts should be justified by cost savings elsewhere, or substantially higher efficiencies such that the long term lower operation costs off-set the higher initial costs. However, a moderate increase in efficiency that can be gained even with large numbers of pumps would likely not make this tradeoff economically worthwhile.

Finally, there is the practical challenge of implementing a system in which a series of distinct chambers hold very different pressures while also allowing solids flow between them. This is especially true for some of the very low pressures considered here. Any sort of moving packed bed between chambers will have a number of engineering challenges to overcome both to controllably move the particles between chambers and to maintain large pressure differences between chambers, especially since the entire configuration will operate at the very highest temperature in the thermochemical system (reduction temperature). Additionally, this type of cascade faces challenges similar to those for the single pressure vacuum case, in which the largest pressure differential occurs between the final chamber (N_C) and the subsequent oxidation step. All of these large pressure differences will be difficult to implement with a continuously flowing solid material, especially at the extremely high temperatures under which the system operates. These challenges will be difficult to overcome, and it is not clear that the gain in system efficiency shown here would justify this difficult and expensive system.

4.3. Practicality of Inert Gas Sweep Reduction

There are a number of challenges to operate a process at any sort of scale at both very high temperatures and at very high or low pressures as discussed above. However, there are also

challenges with removing O₂ using an inert sweep gas; it requires a large amount of sensible heating and cooling for each cycle, it requires separation for each cycle, and a reactor leak would require the inert gas to be re-purified or replaced entirely. There are also practical issues with achieving the thermodynamic productivity shown here. Some issues are related to reaction rates and kinetics; these are discussed elsewhere [4]. Additionally, there are other issues with processing of the inert gas to achieve the very low oxygen partial pressures required for efficiency reduction. Two important issues are the ability of an oxygen separation technology to rapidly achieve the inert gas purity assumed in this work, as well as the ability of the inert gas and solid flows to achieve (or at least approach) the counter-flow arrangement assumed here. Brendelberger *et al.* has found that the latter of these issues may be difficult [17]. These will need to be explored and demonstrated experimentally.

The inert/oxygen separation energy calculated in this work did not make any assumptions on a specific technology, but rather relied on different entropies of mixing for the different streams into and out of the separator. Thus, it does not make any assumptions about the physical ability of a real separator to achieve a particular inert gas purity. Additionally, it does not make any assumptions about the time it would take a separator to achieve a given purity. This will have a large impact on the practicality and system efficiency of an inert gas sweep system. There are currently some commercial products that have demonstrated oxygen purities at temperatures of interest [21, 26], but more information is needed about the limitations of these technologies and the energetic efficiencies they are able to achieve. Further development is likely required to improve upon existing technologies to make this type of operation truly preferable.

5. Conclusions

A thermodynamic model has been used to compare different methods for achieving a low oxygen partial pressure, and the impact that each of these methods has on the system efficiency as a whole. Lower vacuum pump efficiencies are incorporated into the model, and suggest that currently available vacuum pumping results in low STH efficiencies for thermodynamic pump efficiencies of <10%. Meanwhile, a novel recycled inert gas sweep with a high temperature separation step maintains relatively high STH efficiencies over a range of gas purification efficiencies and flow rates. Thermodynamic separation efficiency values of around 10% are also likely to result in high system efficiency capability. Ultimately, the most efficient mode of operation will depend on the efficiency at which the inert gas and oxygen can be separated (in

the inert gas case) and the efficiency at which the vacuum pumps can operate (in the vacuum case). Further, the efficiency of a cascade pressure reduction has been examined, which uses multiple vacuum pumps operating at different pressures to achieve high levels of vacuum. It was found that cascade pressure reduction does increase the effective pump efficiency relative to a single vacuum pump, but this increase (typically a maximum of 5X) is not large enough to cause the system efficiency to overtake the inert gas case. These results suggest that future research should focus on the development of high temperature ionic transport membranes, or other technologies with similar effects, for efficiently separating O₂ from an O₂-containing inert gas sweep stream where the inert gas is recycled to the reduction reactor without having been substantially cooled. Alternately, additional efforts to achieve a thermodynamic vacuum pump efficiency of 10% would drastically increase the possibility of that approach to thermochemical reduction.

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