Maximizing Fuel Production Rates in Isothermal Solar Thermochemical Fuel Production

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ABSTRACT. Production of chemical fuels by isothermal pressure-swing cycles has recently generated significant interest. In this process a reactive oxide is cyclically exposed to an inert gas, which induces partial reduction of the oxide, and to an oxidizing gas of either H₂O or CO₂, which reoxidizes the oxide, releasing H₂ or CO. At sufficiently high temperatures and sufficiently low gas flow rates, both the reduction and oxidation steps become limited only by the flow of gas across the material and not by material kinetic factors. In this contribution, we develop a numerical model describing fuel production rates in this gas-phase limited regime. The implications of this behavior are explored under all possible isothermal pressure-swing cycling conditions, and the outcome is optimized in terms of fuel production rate as well as fuel conversion and utilization of input gas of all types. Fuel production rate is maximized at infinitesimally small cycle times and attains a value that is independent of material thermodynamics. Gas utilization is maximized at infinitesimally small gas inputs, but the values can be made independent of cycle time, depending on manipulation of flow conditions. Gas-phase conditions (temperature, oxidant and reductant gas partial pressures, and CO₂ vs H₂O as oxidant) have a strong impact on fuel production metrics. Under realistic, finite cycle times, material thermodynamics play a measurable role in establishing fuel production rates.

KEYWORDS. Solar fuels, thermochemical cycle, kinetics, thermodynamics, ceria

INTRODUCTION. The storage of solar energy in chemical fuels has been a major research goal of the past decade.[1] Solar-driven two-step thermochemical fuel production has emerged as an attractive route towards this goal by harnessing the high efficiencies, and potentially low costs,

promised by concentrated solar power (CSP).[2] By utilizing the high temperatures inherent to CSP, two-step thermochemical fuel production offers the potential for high solar-to-fuel conversion efficiency, as well as chemical simplicity and straightforward production of a range of fuels, including H₂ and CO [3–6], and even methane [7,8] and syngas [7,9,10] (combination of H₂ and CO), which has been coupled to a Fischer-Tropsch reactor to generate jet fuel.[11,12] In brief, a suitable reactive oxide is reduced in a first step by exposure to high temperature, and in a second step a chemical fuel is generated by exposure of the reduced oxide to steam and/or carbon dioxide. Use of nonstoichiometric oxides, those that undergo changes in oxygen content without changes in crystallographic phase, has enabled sustained cycling as a result of the relatively gentle changes in mechanical state induced by the process. Materials examined include ceria and its doped derivatives [14–18] and perovskite-structured oxides in the (Ln,A)(Mn,Al)O_{3-δ} (Ln = lanthanide and A = alkaline earth metal) family [19–23], and their characteristics are compared in recent reviews [24,25]. Typically, whether employing a phase change oxide or a nonstoichiometric oxide, the fuel production step is carried out at a temperature lower than that of the oxygen release step, although recently, isothermal operation has been demonstrated. [26–29] In all cases, theoretical efficiencies increase monotonically with temperature, [5,16,27] and operating conditions are limited instead by considerations such as heat losses from the reactor and the thermal stability of the reactive oxide itself or of confinement materials. Accordingly, reduction at a temperature as high as 1500 °C is not uncommon. This high temperature operation implies that thermally activated material kinetic parameters, specifically, the surface reaction rate and bulk diffusivity, are very high. In turn, such behavior raises the possibility that the global fuel production rate in thermochemical processes may be limited, not by these material kinetic parameters, but rather by the rate at which the reactant gas supplies gas-phase reactants or removes gas-phase products.[30,31]

Driven by this consideration, we reported in a recent contribution a numerical model that treats the specific case of gas-phase limited fuel production rates under isothermal cycling of a nonstoichiometric oxide.[31] Treatment of the problem in this manner is distinct from approaches which take material kinetic parameters to contribute to rate-limitations.[32,33] The applicability of the model to realistic systems was validated by comparison to experimentally measured reduction and oxidation rates of undoped ceria. Along with a brief description of the model, a limited set of implications of gas-phase limited kinetics was reported. In particular, it was shown

that the global fuel production rate increases monotonically with decreasing cycle time, with maximum theoretical productivity occurring in the limit of an infinitesimal cycle. It was further demonstrated how material choice impacts productivity when the cycling time is finite. In the present work we provide the mathematical basis for the previous results and extend the numerical model to any isothermal pressure-swing cycling condition. Moreover, we consider in the present work optimization with respect to fuel conversion (H_2O to H_2 or CO_2 to CO) as well as fuel production rate. This work provides, for the first time, the theoretical rate and gas utilization limits of solar-driven isothermal pressure-swing cycling under all conditions. This analysis provides guidance for the optimal operating conditions for operational reactors and specifies the benefits of reactive material choice and sizing. While the treatment here remains specific to isothermal pressure-swing cycling, an operational strategy that offers several inherent advantages in terms of thermomechanical simplicity, [27,28] the numerical method is generalizable to accommodate arbitrary swings in both temperature and pressure.

THERMO-KINETIC MODEL. The physical situation of interest, analogous to that described briefly in our previous work[31], is illustrated schematically in Figures 1 and 2. A block of porous, reactive oxide, in this case ceria, is held at a fixed temperature, T_0 (set here at 1500°C) and exposed sequentially to reducing and oxidizing atmospheres, with oxygen non-stoichiometry values cycling between the states represented in Figure 1. The gas compositions are represented by the dashed vertical lines, and the end-states, 1 and 2, are attained under idealized conditions of infinitely large gas supply or infinitely long reaction time. Consistent with the notion of infinitely rapid material kinetics, the oxygen partial pressure at a given time, t , of the gas coming out of the reactor, $P_{\text{O}_2\text{out}}(t)$, is taken to be equal to the oxygen partial pressure of a gas in equilibrium with the material, $P_{\text{O}_2}(\delta, T_0)$, at the nonstoichiometry $\delta(t)$ that the material has attained at time t . In other words, the oxide releases oxygen instantaneously up to the thermodynamic capacity of the gas flowing across the sample, regardless of the kinetic properties of the material. The sample is assumed to be small enough that no stoichiometry gradient exists across it, and the gas flow through the reactor is assumed to be characterized by plug flow. Based on these characteristics, we call this the thermo-kinetic model.

The reduction step is considered first, Figure 2a, during which the material is exposed to an inert gas containing a known, very low quantity of oxygen. This exposure induces reduction from an initial oxygen nonstoichiometry value of δ_i to a final value of δ_f according to the reaction

$$\frac{1}{\Delta\delta_{red}} CeO_{2-\delta_i} \rightarrow \frac{1}{\Delta\delta_{red}} CeO_{2-\delta_f} + \frac{1}{2} O_2 \quad (1)$$

where $\Delta\delta_{red} = \delta_f - \delta_i$. Oxygen mass balance across the reactor requires

$$F_{O_2out} - F_{O_2in} = r_{O_2} \quad (2)$$

where F_{O_2in} and F_{O_2out} are the molar flow rates of oxygen in to and out of the reactor at a specified time, and r_{O_2} is the rate of oxygen generation by the sample. The reduction reaction in Equation (1) implies that the latter term is given by

$$r_{O_2} = \frac{n_{CeO_{2-x}}}{2} \frac{d\delta_{red}}{dt} \quad (3)$$

where $n_{CeO_{2-x}}$ is the number of moles of metal oxide inside the reactor (x is the oxygen nonstoichiometry before the material is placed in the reactor and hereafter is set at zero), and $d\delta_{red}/dt$ is the rate of change of oxygen stoichiometry in the metal oxide, denoted with *red* to indicate reduction. The molar flow rate of oxygen into the reactor is fixed experimentally as

$$F_{O_2in} = \frac{P_{O_2in}}{P_{tot}} F_{red} \quad (4)$$

where P_{O_2in} is the inlet oxygen partial pressure, P_{tot} is the total pressure, set at 1 atm, and F_{red} is the total inlet molar flow rate of gas during reduction.

Under the assumption that the oxygen partial pressure of the outlet stream is determined by the nonstoichiometry of the material, the molar flow rate of oxygen out of the reactor is simply

$$F_{O_2out} = \frac{P_{O_2}(\delta, T_0)}{P_{tot}} F_{out} \quad (5)$$

where $P_{O_2}(\delta, T_0)$ is the equilibrium oxygen partial pressure of a gas in equilibrium with the metal oxide at a nonstoichiometry of δ . The total outlet flow rate, F_{out} will be the sum of the inlet flow rate, F_{red} , and the oxygen generated within the reactor, r_{O_2} , as given in Eq. (3). With Equation (5) this implies

$$F_{O_2out} = \frac{P_{O_2}(\delta, T_0)}{P_{tot}} \left(F_{red} + \frac{n_{CeO_2}}{2} \frac{d\delta_{red}}{dt} \right) \quad (6)$$

Combining Equations (2) through (6) and solving for $d\delta_{red}/dt$ gives

$$\frac{d\delta_{red}}{dt} = \frac{2F_{red}}{n_{CeO_2}} \frac{(P_{O_2}(\delta, T_0) - P_{O_2in})}{(P_{tot} - P_{O_2}(\delta, T_0))} \quad (7)$$

in which the only unknown is $P_{O_2}(\delta, T_0)$. If the thermodynamics of reduction of the material, that is, the enthalpy and entropy of the reduction reaction expressed in Equation (1) ($\Delta H_{red}(\delta)$ and $\Delta S_{red}(\delta)$, respectively) have been determined, then $P_{O_2}(\delta, T_0)$ can be calculated according to

$$\frac{1}{2} \ln \left(P_{O_2}(\delta, T) \right) = \frac{-\Delta H_{red}(\delta) + T \Delta S_{red}(\delta)}{RT} \quad (8)$$

With Equations (7) and (8) the evolution of nonstoichiometry during reduction can be determined as a function of time via an iterative treatment. The volumetric oxygen production (relevant as this is the quantity typically detected by measurement of the composition of the outlet gas stream) is directly proportional to the rate of change in nonstoichiometry. On a per mass of oxide basis, it is given as

$$\dot{v}_{O_2}(t) = \frac{V_M}{2M_{CeO_{2-x}}} \frac{d\delta_{red}}{dt} \quad (9)$$

where V_M is the molar volume of oxygen and $M_{CeO_{2-x}}$ is the molecular mass of ceria at the nonstoichiometry of the material before being placed into the reactor, x (again, taken to be zero hereafter).

The behavior under oxidation, Figure 2b, is governed by the reaction

Here it is presumed that the oxygen content at the initiation of the oxidation reaction is equal to that at the completion of the reduction reaction, and vice versa, a situation that applies to steady state cycling. In addition, the water supplied to the reactor for the oxidation step can undergo thermolysis according to

with an equilibrium constant at the reactor temperature T_0 of K_{H_2O, T_0} . Thus, characterization of the reactor in the fuel production step will require material balances on water, hydrogen, and oxygen similar to that expressed in Equation (2).

The inlet flow of gas in the oxidation step is delivered at a constant flow rate, F_{ox} , and is a mixture of only inert gas and water with a fixed mole fraction of water, χ_{H_2O} . Accordingly,

$$F_{H_2Oin} = \chi_{H_2O} F_{ox} \quad (12)$$

where F_{H_2Oin} is the total inlet molar flow rate of water during oxidation. After entering the reactor, water is consumed both by reaction with the oxide and by thermolysis. The combined extent of consumption is designated ψ , the extent of reaction of water. With ψ so defined, the flow rate of water out of the reactor becomes

$$F_{H_2Oout} = (1 - \psi)F_{H_2Oin} \quad (13)$$

Because consumption of water by either Equation (10) (oxide oxidation) or (11) (thermolysis) directly results in generation of hydrogen, the flow rate of hydrogen out of the reactor is

$$F_{H_2out} = \psi F_{H_2Oin} \quad (14)$$

In the case of oxygen, generation occurs via Equation (11), but due to consumption of water via Equation (10), the amount of oxygen flowing out of the reactor is less than what would be expected from thermolysis alone. Balancing these factors yields

$$F_{O_2out} = \frac{\psi}{2} F_{H_2Oin} + \frac{n_{CeO_2}}{2} \frac{d\delta_{ox}}{dt} \quad (15)$$

The total molar flow rate out of the reactor, F_{out} , is simply the total coming in, modified by the additional flows due to oxygen and hydrogen production and the loss of flow due to water consumption:

$$F_{out} = F_{ox} + F_{O_2out} + F_{H_2out} - \psi F_{H_2Oin} = F_{ox} + F_{O_2out} \quad (16)$$

Inserting the definition of F_{O_2out} given in Eq. (15) into the above yields

$$F_{out} = F_{ox} + \frac{\psi}{2} F_{H_2Oin} + \frac{n_{CeO_2}}{2} \frac{d\delta_{ox}}{dt} \quad (17)$$

The unknown quantity F_{out} is eliminated by recognizing that, as before, in the limit of infinitely fast material kinetics the oxygen partial pressure of the outlet stream is determined by the nonstoichiometry of the material, Equation (5). Inserting Equations (5), (12), and (15) into (17), and solving for $d\delta_{ox}/dt$ yields

$$\frac{d\delta_{ox}}{dt} = \frac{F_{ox}}{n_{CeO_2}} \frac{(2P_{O_2}(\delta, T_0) - \psi \chi_{H_2O}(P_{tot} - P_{O_2}(\delta, T_0)))}{(P_{tot} - P_{O_2}(\delta, T_0))} \quad (18)$$

This expression for $d\delta_{ox}/dt$ is analogous to Equation (7) for the rate of nonstoichiometry change under reducing conditions. However, it contains the unknown ψ . This quantity can be determined given the additional constraint that the outlet gases must be at equilibrium with the water thermolysis reaction and thus

$$K_{H_2O, T_0} = \frac{P_{H_2out} P_{O_2}(\delta, T_0)^{\frac{1}{2}}}{P_{H_2Oout} P_{ref}^{\frac{1}{2}}} = \left(\frac{\psi}{1 - \psi} \right) P_{O_2}(\delta, T_0)^{\frac{1}{2}} \quad (19)$$

where the reference pressure P_{ref} is taken as 1 atm. Combining Equations (18) and (19) and eliminating ψ gives an expression for $d\delta_{ox}/dt$ that depends only on $P_{O_2}(\delta, T_0)$

$$\frac{d\delta_{ox}}{dt} = \frac{F_{ox}}{n_{CeO_2}} \frac{\left(2P_{O_2}(\delta, T_0)^{\frac{3}{2}} + 2P_{O_2}(\delta, T_0)K_{H_2O, T_0} - \chi_{H_2O}K_{H_2O, T_0}(P_{tot} - P_{O_2}(\delta, T_0)) \right)}{\left(P_{O_2}(\delta, T_0)^{\frac{1}{2}} + K_{H_2O, T_0} \right) (P_{tot} - P_{O_2}(\delta, T_0))} \quad (20)$$

As in the case of oxygen release, the hydrogen production is directly proportional to the rate of nonstoichiometry change, and is given by

$$\dot{v}_{H_2}(t) = -\frac{V_M}{M_{CeO_2}} \frac{d\delta_{ox}}{dt} \quad (21)$$

We note that expressions essentially identical to (7) and (18) were reported independently by Venstrom et al.[30] Our work presents a complete derivation of these expressions.

RESULTS AND DISCUSSION. The expressions in Eqs. (7), (9), (20), and (21), given in our previous work without derivation, permit computation of the gas release profiles by the thermokinetic model and were shown to match the experimental profiles obtained from ceria at high temperatures and moderate gas flow rates. For convenience, the experimental tests were conducted using an oxidation atmosphere of 20% steam. However, further computational analysis was performed for oxidation by pure steam atmosphere, a condition also applied in this work. This change was made for the following reasons. It is readily appreciated that on thermodynamic grounds more hydrogen is expected per cycle if pure steam is utilized for the oxidation gas, up to 5.1 mL g⁻¹ vs. no more than 4.3 mL g⁻¹ under 20% steam. Furthermore, operation under 100% steam eliminates the need to heat and cool inert carrier gas, providing another advantage. Beyond these immediate aspects, pure steam also results in higher gas release rates during both reduction and oxidation, even when the H₂O flow rates are identical (SI Figure S1).

One can use results of computations with Eqs. (7), (9), (20), and (21) to maximize a range of outputs pertinent to hydrogen cost minimization, such as average fuel production rate or reactant to fuel conversion, with respect to a range of control variables such as gas composition, cycle time, or gas flow rate. For example, due to the diminishing rate of fuel production with time, an optimal cycle will employ finite and possibly very short reaction times to minimize the cost of producing hydrogen. In what follows, the average fuel production rate is optimized analytically (as opposed to only computationally[31]) in terms of reduction and oxidation cycle times for given reduction and oxidation gas flow rates. For these optimal cycling conditions, the production rate is then optimized with respect to the gas flow rates to determine a global maximum production rate for a given reduction and oxidation gas composition and reactor temperature. A similar analysis is then performed for optimization of gas utilization and related back to the production rate optimization.

We then optimize the production rate for any given total cycle length and demonstrate the implications of this analysis for experimental tests. As a result, we identify the ideal production rate metric to compare with experimental results and examine how the global maximum of the production rate by this metric depends on gas composition and reactor temperature.

Optimization of Cycle Times for Rate.

Identification of the optimal cycling for fuel production rate requires an expression for this rate, as averaged over the complete cycle. As noted, under steady state cycling the nonstoichiometry at the end of the oxidation portion of the cycle will be equal to that at the initiation of the reduction step and vice versa, implying

$$\Delta\delta = \Delta\delta_{red} = -\Delta\delta_{ox}(= \delta_f - \delta_i) \quad (22)$$

The average rate of hydrogen production, $\bar{v}_{H_2}$, as evaluated over a complete such cycle is directly proportional to this change in oxygen stoichiometry and inversely proportional to the total cycle time. Specifically, it is given by

$$\bar{v}_{H_2} = \frac{V_M}{M_{CeO_2}} \frac{\Delta\delta}{t_{red} + t_{ox}} \quad (23)$$

The changes in stoichiometry over the specified reduction (t_{red}) and oxidation (t_{ox}) cycle times are, in addition to being equal, respectively expressed as

$$\Delta\delta_{red} = \int_0^{t_{red}} \frac{d\delta_{red}}{dt} dt \quad (24)$$

$$\Delta\delta_{ox} = \int_{t_{red}}^{t_{red}+t_{ox}} \frac{d\delta_{ox}}{dt} dt \quad (25)$$

where the respective rate terms are given in Equations (7) and (20).

From Equation (23) it is apparent that the hydrogen production rate will depend on t_{red} and t_{ox} , and some optimal pair of values may exist which maximize $\bar{v}_{H_2}$. In principle, Equations (24) and (25) can be directly used to calculate the average rate of hydrogen production as a function of reduction and oxidation times, but such an approach is computationally intensive because determination of δ_i and δ_f from a given t_{red} and t_{ox} must be accompanied by an iterative calculation to satisfy the steady-state condition. An alternative analysis is possible by recognizing that $d\delta/dt$ is a function of only δ , implying

$$t_{red} = \int_{\delta_i}^{\delta_f} \left(\frac{d\delta_{red}}{dt} \right)^{-1} d\delta \quad (26)$$

$$t_{ox} = \int_{\delta_f}^{\delta_i} \left(\frac{d\delta_{ox}}{dt} \right)^{-1} d\delta \quad (27)$$

Using these relationships, it is straightforward to calculate t_{red} and t_{ox} for a given steady-state set $\{\delta_i, \delta_f\}$.

Although maximization of the hydrogen production rate can be performed in terms of optimal values of t_{red} and t_{ox} , because $t_{red} + t_{ox}$ appears in the expression of $\bar{v}_{H_2}$ (Eq. (23)), it is more natural to maximize $\bar{v}_{H_2}$ over a basis set that includes this summed term. Selected here are the linearly independent variables of the set $\{t_{tot}, f_{red}\}$ defined respectively according to

$$t_{tot} = t_{red} + t_{ox} \quad (28)$$

$$f_{red} = \frac{t_{red}}{t_{red} + t_{ox}} \quad (29)$$

where t_{tot} is the total cycle time and is defined in the range $(0, \infty)$, and f_{red} is the fraction of time allotted to reduction, defined in the range $(0, 1)$. It is noted that for each $\{t_{tot}, f_{red}\}$ pair, the calculation implies a unique, corresponding $\{\delta_i, \delta_f\}$ pair.

Evaluation of $\bar{v}_{H_2}$ for every $\{t_{tot}, f_{red}\}$ pair with a given set of reduction and oxidation conditions and amount of material in the reactor reveals that the maximum value of $\bar{v}_{H_2}$ is achieved as t_{tot} approaches 0. This result (that $\bar{v}_{H_2}$ is maximized at $t_{tot} \rightarrow 0$), shown in our previous work to be true for a specific set of conditions,[31] can be shown to be a maximum irrespective of the values of the process variables and material and gas thermodynamic properties (see SI). Thus, $\bar{v}_{H_2}(t_{tot} \rightarrow 0)$ represents an important limit. The average hydrogen production per cycle for the instantaneous cycling represented by this condition reduces to

$$\bar{v}_{H_2}(t_{tot} \rightarrow 0) = \lim_{t_{tot} \rightarrow 0} \left(\frac{V_M}{M_{CeO_2}} \frac{\Delta\delta}{t_{tot}} \right) = \frac{V_M}{M_{CeO_2}} f_{red} \left(\frac{d\delta_{red}}{dt} \right) = - \frac{V_M}{M_{CeO_2}} (1 - f_{red}) \left(\frac{d\delta_{ox}}{dt} \right) \quad (30)$$

Here, because of the infinitesimally small cycle time, the entire process occurs at a single value of δ . That is, it occurs at $\delta_i = \delta_f = \delta^*$. Moreover, it can be shown that, for a given f_{red} , only one δ^* will satisfy Equation (30), and that this δ^* corresponds to the $P_{O_2}(\delta^*, T_0)$ which, in turn, satisfies

$$f_{red} F_{red} \frac{2(P_{O_2}(\delta^*, T_0) - P_{O_2 in})}{(P_{tot} - P_{O_2}(\delta^*, T_0))} =$$

$$-(1 - f_{red}) F_{ox} \frac{\left(2P_{O_2}(\delta^*, T_0)^{\frac{3}{2}} + 2P_{O_2}(\delta^*, T_0) K_{H_2O, T_0} - \chi_{H_2O} K_{H_2O, T_0} (P_{tot} - P_{O_2}(\delta^*, T_0)) \right)}{\left(P_{O_2}(\delta^*, T_0)^{\frac{1}{2}} + K_{H_2O, T_0} \right) (P_{tot} - P_{O_2}(\delta^*, T_0))} \quad (31)$$

obtained from inserting Equations (7) and (20) into (30). The above holds for the $t_{tot} \rightarrow 0$ limit, but does not specify the value of f_{red} . In order to maximize the hydrogen production rate, f_{red} is set to the optimal value, $f_{red}^{opt}(t_{tot} \rightarrow 0)$, [31] in which case the hydrogen production rate becomes

$$\bar{v}_{H_2}(t_{tot} \rightarrow 0) = \frac{v_M}{m_{CeO_2}} \left(f_{red}^{opt}(t_{tot} \rightarrow 0) \right) F_{red} \frac{2(P_{O_2}(\delta^{*opt}, T_0) - P_{O_2 in})}{(P_{tot} - P_{O_2}(\delta^{*opt}, T_0))} \quad (32)$$

where m_{CeO_2} is the mass of ceria in the reactor ($m_{CeO_2} = M_{CeO_2} n_{CeO_2}$), and for notational ease, only the result obtained from considering the reduction is reported; an analogous result can be expressed from considering the oxidation.

Notably, the value of $P_{O_2}(\delta^*, T_0)$ defined by Eq. (31) is *entirely independent* of the properties of the reactive oxide. That is, although the δ^* that corresponds to $P_{O_2}(\delta^*, T_0)$ depends on the material redox thermodynamics, $P_{O_2}(\delta^*, T_0)$ depends only on the process parameters (f_{red} , F_{red} , F_{ox} , P_{tot} , $P_{O_2 in}$, χ_{H_2O}) and the thermodynamic properties of the gases (K_{H_2O, T_0} , or the analogous dissociation constant for CO_2). Accordingly, the $P_{O_2}(\delta^{*opt}, T_0)$, the value of $P_{O_2}(\delta^*, T_0)$ that satisfies Eq. (31) when f_{red} is $f_{red}^{opt}(t_{tot} \rightarrow 0)$, is also independent of the properties of the reactive oxide. Consequently, the optimized hydrogen production, Eq. (32), exhibits a dependence on material properties only via the molecular mass of the oxide. Recasting this expression for normalization on a per mole of oxide basis renders the result entirely independent of material choice. This result provides the mathematical foundation for the observation obtained computationally in our previous work [31] that the maximum productivity is material independent.

Optimization of Gas Flow Rates for Fuel Production Rate.

The analysis to this point takes the reduction and oxidation gas flow rates to be fixed. The next step in the optimization is to vary these terms. Consideration of the rate expressions for the change in stoichiometry, Eqs. (7) and (20), reveals that the gas production rates (volumetric gas flow rate per gram of oxide) can be made arbitrarily large by simply increasing the inlet gas flow rate or decreasing the amount of oxide in the reactor. Thus, an alternative metric for optimization, which does not suffer from this arbitrary behavior and can thus reveal fundamental performance

differences between oxide materials (which appear away from the $t_{tot} \rightarrow 0$ limit), is required. In our earlier work, we introduced the nondimensional characteristic hydrogen production rate[31] defined by

$$\bar{Q} = \frac{\bar{v}_{H_2} m_{CeO_2}}{V_M F_{tot}} = \frac{n_{CeO_2}}{F_{tot}} \frac{\Delta\delta}{t_{tot}} \quad (33)$$

where

$$F_{tot} = F_{red} + F_{ox} \quad (34)$$

and for completeness we define the quantity

$$\Phi = \frac{F_{red}}{F_{red} + F_{ox}} \quad (35)$$

As described previously, $\bar{Q}$ is the hydrogen production rate normalized to the combined flow rates of the oxidation and reduction gases, F_{tot} ; $\bar{Q}$ is independent of both this total flow rate and the total mass of oxide in the reactor.

Inserting the above definitions of Φ and F_{tot} into Equation (31) yields

$$f_{red} \Phi^{\frac{2(P_{O_2}(\delta^*, T_0) - P_{O_2, in})}{(P_{tot} - P_{O_2}(\delta^*, T_0))}} = -(1 - f_{red})(1 - \Phi) \frac{\left(2P_{O_2}(\delta^*, T_0)^{\frac{3}{2}} + 2P_{O_2}(\delta^*, T_0)K_{H_2O, T_0} - \chi_{H_2O}K_{H_2O, T_0}(P_{tot} - P_{O_2}(\delta^*, T_0)) \right)}{\left(P_{O_2}(\delta^*, T_0)^{\frac{1}{2}} + K_{H_2O, T_0} \right)(P_{tot} - P_{O_2}(\delta^*, T_0))} \quad (36)$$

where each side of Equation (36) is equal to $\bar{Q}(t_{tot} \rightarrow 0)$. Significantly, the total flow rate, F_{tot} , falls out of the expression and hence plays no role in setting the optimal relative cycle times or relative gas flow rates in the $t_{tot} \rightarrow 0$ limit. Moreover, as noted in the preceding section, for given values of the process parameters f_{red} , Φ , P_{tot} , $P_{O_2, in}$, and χ_{H_2O} , the value of $P_{O_2}(\delta^*, T_0)$ is uniquely determined and independent of material choice, rendering $\bar{Q}(t_{tot} \rightarrow 0)$ independent of material. As already noted, $P_{O_2}(\delta^*, T_0)$, in turn, defines a unique δ^* specific to the choice of material, which then accompanies each value of $\bar{Q}(t_{tot} \rightarrow 0)$.

The behavior of $\bar{Q}(t_{tot} \rightarrow 0)$ as a function of f_{red} and Φ is presented in relief and contour plots in Figure 3. The results, as captured in the contour plot in particular, reflect the symmetry of Eq. (36), in which f_{red} and Φ are mathematically interchangeable. Significantly, it is apparent that $\bar{Q}(t_{tot} \rightarrow 0)$ displays a single global maximum, $\bar{Q}^{max}$, and that this occurs at f_{red} and Φ values denoted as $f_{red}^{max} = \Phi^{max} = 0.57$, and at an oxygen partial pressure denoted as $P_{O_2}^{max} = P_{O_2}(\delta^{*max}, T_0)$. Because the other parameters in Equation (36) depend only on the properties of the carrier gases, this global maximum, amounting to 2.4×10^{-4} , represents the maximum value of $\bar{Q}$ for any cycling conditions for the given set of carrier gases and temperature of operation,

irrespective of the material utilized. The value of $P_{O_2}^{max}$ under these conditions is 3.8×10^{-4} atm. The symmetry of Eq. (36) moreover implies that even when gas composition and temperature are varied, $\bar{Q}^{max}$ always occurs when $f_{red} = \Phi$, and that the value of f_{red} (and Φ) is determined solely by the properties of the gases (see SI). It should be noted that the optimal f_{red} and Φ described here are significantly different from the experimentally optimized values for CO production ($f_{red} = 0.39$, $\Phi = 0.75$).[28] However, in the experimental study, the cycling conditions were optimized for maximum thermal efficiency, including the heat load of reduction and oxidation gases, rather than fuel productivity alone, and a different optimal condition is to be expected.

Optimization of Gas Flow Rates for Flow Utilization.

The metrics $\bar{Q}$ and $\bar{v}_{H_2}$ describe the hydrogen production rate and imply maximization of $\Delta\delta/t_{tot}$, the average rate of change of the oxygen nonstoichiometry. In an overall cost optimization of fuel production, this type of metric affects any time-based cost inputs, such as solar derived thermal energy. Alternatively, one may wish to maximize fuel production relative to the quantity of input gases used to generate the hydrogen, *i.e.*, the gas utilization. In this case, the maximization is performed on $\Delta\delta/N$, where N is some measure (at this point arbitrary) of the number of moles of gas used over a complete cycle. This type of metric accounts for cost inputs based on the amount of gas used, such as the manufacturing and heating costs of the gases.

The simplest definition of N for maximization of gas utilization is N_{tot} , the sum of the moles of gas used during reduction (N_{red}) and during oxidation (N_{ox}), an approach that treats the cost of reduction gas to be the same as that of the oxidation gas. The molar quantity of hydrogen produced during a cycle per unit N_{tot} (the cycle-averaged total gas utilization) is simply

$$\bar{U}_{N_{tot}} = n_{CeO_2} \frac{\Delta\delta}{N_{tot}} \quad (37)$$

Defining $\bar{F}$ as the average molar flow rate of input gases, $\bar{F} = N_{tot}/t_{tot}$, the above can be expressed as

$$\bar{U}_{N_{tot}} = \frac{n_{CeO_2}}{\bar{F}} \frac{\Delta\delta}{t_{tot}} \quad (38)$$

Inserting the definition of $\Delta\delta/t_{tot}$ implied by Eq. (23) yields

$$\bar{U}_{N_{tot}} = \frac{\bar{v}_{H_2} m_{CeO_2}}{V_M \bar{F}} \quad (39)$$

an expression similar in functional form to that of $\bar{Q}$ (Eq. (33)). The flow rate terms $\bar{F}$ and F_{tot} in the two optimization quantities are readily related to one another by noting

$$N_{tot} = N_{red} + N_{ox} \quad (40)$$

$$N_{red} = F_{red} t_{red} = (f_{red} \Phi) F_{tot} t_{tot} \quad (41)$$

$$N_{ox} = ((1 - f_{red})(1 - \Phi)) F_{tot} t_{tot} \quad (42)$$

Combined, Equations (40) through (42) along with the definition of $\bar{F}$ imply

$$\bar{F} = \theta_{N_{tot}} F_{tot} \quad (43)$$

where

$$\theta_{N_{tot}} = (f_{red} \Phi + (1 - f_{red})(1 - \Phi)) \quad (44)$$

From Eqs. (33), (39) and (43) it is apparent that $\bar{U}_{N_{tot}}$ is directly related to $\bar{Q}$ according to

$$\bar{U}_{N_{tot}} = \bar{Q} / \theta_{N_{tot}} \quad (45)$$

It can be shown that maximization of $\bar{U}_{N_{tot}}$ will occur as $N_{tot} \rightarrow 0$ (see SI); the argument is analogous to that which leads to the conclusion that maximization of $\bar{v}_{H_2}$ occurs as $t_{tot} \rightarrow 0$. Because N_{tot} is defined by three independent variables

$$N_{tot} = \theta_{N_{tot}} F_{tot} t_{tot} \quad (46)$$

the $N_{tot} \rightarrow 0$ limit is accessible three different ways. The first, $F_{tot} \rightarrow 0$, is a trivial case not considered further. The second, $t_{tot} \rightarrow 0$, yields

$$\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0) = \bar{Q}(t_{tot} \rightarrow 0) / \theta_{N_{tot}} \quad (47)$$

for arbitrary values of F_{tot} and $\theta_{N_{tot}}$. Thus, $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ for this case is easily derived from $\bar{Q}(t_{tot} \rightarrow 0)$, given in Equation (36) and depicted in Figure 3. The third case that leads to $N_{tot} \rightarrow 0$ is that in which $\theta_{N_{tot}} \rightarrow 0$, a condition which arises when $f_{red} \rightarrow 0$ and $\Phi \rightarrow 1$, or vice versa. Physically, these conditions correspond to the situation in which, for example, the *time* devoted to *reduction* is infinitesimally small (with arbitrary flow rate) and the *flow* devoted to *oxidation* is also infinitesimally small (with arbitrary oxidation time). Because $\bar{U}_{N_{tot}}$ is a function of N_{tot} and not independently a function of the terms F_{tot} , t_{tot} , and $\theta_{N_{tot}}$ that comprise N_{tot} (see SI), the manner in which $N_{tot} \rightarrow 0$ is achieved has no impact on the resulting $\bar{U}_{N_{tot}}$. Thus, the expression given in Equation (47) also applies when $\theta_{N_{tot}} \rightarrow 0$, and F_{tot} and t_{tot} adopt arbitrary values.

The behavior of $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ as a function of f_{red} and Φ is presented as a contour plot in Figure 4a. In contrast to $\bar{Q}(t_{tot} \rightarrow 0)$, which displays only a single maximum, it is found that $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ is maximized along a line of values of f_{red} and Φ which satisfy the condition

$$\frac{f_{red}\Phi}{f_{red}\Phi + (1-f_{red})(1-\Phi)} = 0.60 \quad (48)$$

where the left hand side of Eq. (48) is the mole fraction of reduction gas, defined by

$$\xi_{red} = \frac{N_{red}}{N_{tot}} \quad (49)$$

Beyond the existence of a line of maximal values of $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ at $\xi_{red} = 0.60$, each of the contour lines of $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ also occurs at a fixed value of ξ_{red} . This behavior can be understood by recognizing that the result of dividing Eq. (36) by $\theta_{N_{tot}}$ (to obtain expressions for $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$) can be written as

$$\xi_{red} \frac{2(P_{O_2}(\delta^*, T_0) - P_{O_2, in})}{(P_{tot} - P_{O_2}(\delta^*, T_0))} = -(1 - \xi_{red}) \frac{\left(2P_{O_2}(\delta^*, T_0)^{\frac{3}{2}} + 2P_{O_2}(\delta^*, T_0)K_{H_2O, T_0} - \chi_{H_2O}K_{H_2O, T_0}(P_{tot} - P_{O_2}(\delta^*, T_0)) \right)}{\left(P_{O_2}(\delta^*, T_0)^{\frac{1}{2}} + K_{H_2O, T_0} \right)(P_{tot} - P_{O_2}(\delta^*, T_0))} \quad (50)$$

Thus, $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ depends only on the single parameter ξ_{red} , and not independently on any of the flow parameters. In accordance with this characteristic of $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$, the results presented in Figure 4a are replotted in Figure 4b as a function of ξ_{red} . The peak in $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ at $\xi_{red} = 0.60$, denoted ξ_{red}^{max} , is prominent in this presentation of the results. Under these conditions, $\bar{U}_{N_{tot}}$ is fully maximized (denoted $\bar{U}_{N_{tot}}^{max}$) and has a value of 4.8×10^{-4} . It should be noted that for the $N_{tot} \rightarrow 0$ case in which $\theta_{N_{tot}} \rightarrow 0$, the quantity $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ only exists (by definition) in the $f_{red} \rightarrow 0, \Phi \rightarrow 1$ and $f_{red} \rightarrow 1, \Phi \rightarrow 0$ corners of Figure 4a. However, even in these limits, ξ_{red} can be varied, tracing the curve of Figure 4b. Thus, the entire range of $\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$ values are represented.

It can be shown that the value of ξ_{red}^{max} is fundamentally controlled by the autodissociation reaction governing the concentration of oxygen in the reactor (e.g., Equation (11) in the case of steam). For the generalized reaction

and operation of a reactor under typical conditions and a temperature of 1500 °C or higher, ξ_{red}^{max} will approximately follow the relation (see SI)

$$\frac{\xi_{red}^{max}}{(1-\xi_{red}^{max})} = 1 + n \quad (52)$$

For the dissociation of either steam or carbon dioxide, each of which have $n = 1/2$, the result is $\xi_{red}^{max} = 0.60$.

From Eq. (45) it is evident that the set of f_{red} and Φ values that maximize $\bar{U}_{N_{tot}}$ will not simultaneously maximize $\bar{Q}$. Specifically, it has been shown above that $\bar{Q}^{max}$ occurs when $f_{red} = \Phi = 0.57$, but this pair of values violates the condition that $\xi_{red} = 0.60$, Eq. (48), required of the $\{f_{red}, \Phi\}$ pair that will maximize $\bar{U}_{N_{tot}}$. However, because $f_{red} = \Phi = 0.57$ implies a ξ_{red} of 0.637, not far from 0.60, and because $\bar{U}_{N_{tot}}$ is not a steep function of ξ_{red} , $\bar{U}_{N_{tot}}(\xi_{red} = 0.637)$ is less than 0.4% smaller than $\bar{U}_{N_{tot}}(\xi_{red}^{max})$ for the conditions of Figure 4a. At different temperatures and gas compositions, the values of f_{red} and Φ that maximize $\bar{Q}$ must, at a minimum, meet the condition $f_{red} = \Phi$ (as already discussed), and the $\bar{U}_{N_{tot}}$ obtained will continue to be governed by Eq. (45). Given the form of $\Theta_{N_{tot}}$ relating $\bar{Q}$ and $\bar{U}_{N_{tot}}$, simultaneous maximization of both these quantities can only occur when $\xi_{red}^{max} = 0.5$ and $\bar{Q}^{max}$ occurs at $f_{red} = \Phi = 0.5$. This situation is not possible when ξ_{red}^{max} is dominated by the autodissociation reaction of steam or carbon dioxide (at which Equation (52) holds), implying one must select f_{red} and Φ values that either optimize rate or gas utilization (but not both), even when operating in the $t_{tot} \rightarrow 0$ limit.

Yet another meaningful optimization is that in which one minimizes the moles of steam (or carbon dioxide) used in the fuel production process while treating the reduction gas effectively as ‘free’, *i.e.*, one maximizes the steam to fuel conversion ratio. In this case, N is N_{H_2O} , which for arbitrary steam concentrations (considered for completeness), is

$$N_{H_2O} = \chi_{H_2O} N_{ox} \quad (53)$$

In analogy to the treatment of optimization against N_{tot} , one obtains the optimization quantity

$$\bar{U}_{N_{H_2O}} = n_{CeO_2} \frac{\Delta\delta}{N_{H_2O}} \equiv \bar{C}_{H_2O} \quad (54)$$

which is recognized as the cycle-averaged steam-to-hydrogen conversion rate and is denoted $\bar{C}_{H_2O}$.

Defining $\bar{F}_{H_2O}$ as the average molar flow rate of reactant gas, $\bar{F}_{H_2O} = N_{H_2O}/t_{tot}$, and continuing the analogy to the treatment of $\bar{U}_{N_{tot}}$, the above can be expressed as

$$\bar{C}_{H_2O} = \frac{\bar{v}_{H_2} m_{CeO_2}}{V_M \bar{F}_{H_2O}} \quad (55)$$

The flow rate terms, $\bar{F}_{H_2O}$ and F_{tot} , are related through the factor

$$\theta_{N_{H_2O}} = \chi_{H_2O}(1 - f_{red})(1 - \Phi) \quad (56)$$

which, on insertion into (55), implies

$$\bar{C}_{H_2O} = \bar{Q}/\theta_{N_{H_2O}} \quad (57)$$

The steam-to-hydrogen conversion ratio can also be expressed in terms of the total gas utilization according to

$$\bar{C}_{H_2O} = \frac{\bar{U}_{N_{tot}}}{\chi_{H_2O}(1 - \xi_{red})} \quad (58)$$

In continued analogy to $\bar{U}_{N_{tot}}$ (i) maximization of $\bar{C}_{H_2O}$ occurs when $N_{H_2O} \rightarrow 0$; (ii) the condition $N_{H_2O} \rightarrow 0$ will be obtained when $t_{tot} \rightarrow 0$, $\theta_{N_{H_2O}} \rightarrow 0$, or, the trivial case, $F_{tot} \rightarrow 0$; (iii) evaluation of $\bar{C}_{H_2O}(N_{H_2O} \rightarrow 0)$ is possible directly from $\bar{Q}(t_{tot} \rightarrow 0)$; and (iv) the result holds true at arbitrary t_{tot} so long as $\theta_{N_{H_2O}} \rightarrow 0$, which occurs when $f_{red} \rightarrow 1$ or $\Phi \rightarrow 1$, or both.

The behavior of $\bar{C}_{H_2O}(N_{H_2O} \rightarrow 0)$ with $\chi_{H_2O} = 1$ is presented as a function of f_{red} and Φ in Figure 4c, and as a function of ξ_{red} in Figure 4d. From the form of Eq. (58) it is apparent that $\bar{C}_{H_2O}$, like $\bar{U}_{N_{tot}}$, depends only on the single parameter ξ_{red} , and not independently on any of the flow parameters, justifying the representation in Figure 4d. For the $N_{H_2O} \rightarrow 0$ case resulting from $\theta_{N_{H_2O}} \rightarrow 0$, $\bar{C}_{H_2O}(N_{H_2O} \rightarrow 0)$ only exists (by definition) in the $f_{red} \rightarrow 1$ or $\Phi \rightarrow 1$ limits of Figure 4c. Furthermore, $\bar{C}_{H_2O}$ reaches a maximum value as $\xi_{red} \rightarrow 1$, which can happen when f_{red} and/or Φ approach 1. In this limit, each cycle consists almost purely of reduction, and the δ^* at which the material operates is equal to the maximally reduced value, that which is in equilibrium with the inlet oxygen partial pressure during reduction, P_{O_2in} . This behavior arises because no penalty is associated with the use of the reduction gas. Thus, the maximum value of $\bar{C}_{H_2O}$ is achieved when the oxidation rate (for a given amount of oxidizing gas) is maximized, regardless of how much reducing gas is required to reach this rate. This highest oxidation rate, in turn, occurs when the material is the most reduced, and its non-stoichiometry corresponds to the equilibrium with $P_{O_2}(\delta, T_0) = P_{O_2in}$. Accordingly, the maximum $\bar{C}_{H_2O}$, $\bar{C}_{H_2O}^{max}$, is given by the simple thermodynamic calculation

$$\bar{C}_{H_2O}^{max} = \frac{P_{O_2in}^{\frac{1}{2}}}{K_{H_2O, T_0}} \quad (59)$$

and has a value of 1.29×10^{-2} for the conditions considered. Significantly, this maximal steam-to-hydrogen conversion ratio is entirely independent of material thermodynamics.

The two terms $\bar{U}_{N_{tot}}$ and $\bar{C}_{H_2O}$ imply specific relative weights to the costs of reduction and oxidation gases: in the case of $\bar{U}_{N_{tot}}$ the two gases are equally weighted, whereas in the case of $\bar{C}_{H_2O}$ the reduction gas is free and the oxidation gas is the only relevant quantity. A generalized treatment allows for arbitrary relative weights to reflect the ‘true’ system costs of providing the two gas streams. In such a case, the appropriate N against which to perform the optimization is the weighted term

$$N_w = w_{red}N_{red} + w_{ox}N_{ox} \quad (60)$$

where w_{red} and w_{ox} are (unitless) weighting terms that reflect, in a generic sense, the respective molar costs of the reduction and oxidation gas. Inserting the expressions for N_{red} and N_{ox} from Equations (41) and (42), respectively, into N_w yields

$$N_w = (w_{red}f_{red}\Phi + w_{ox}(1 - f_{red})(1 - \Phi))F_{tot}t_{tot} \quad (61)$$

And the cost-weighted gas utilization is given as

$$\bar{U}_w = \bar{Q}/\theta_{N_w} \quad (62)$$

where

$$\theta_{N_w} = (w_{red}f_{red}\Phi + w_{ox}(1 - f_{red})(1 - \Phi)) \quad (63)$$

Optimization of $\bar{U}_w$ would then represent the most cost-effective use of the reduction and oxidation gases in the gas-phase limited regime.

To briefly summarize the results to this point, the analysis has revealed the following properties of isothermal cycling: The fuel production rate is maximized with respect to cycling time in the limit $t_{tot} \rightarrow 0$; it is fully maximized when the fraction of time dedicated to reduction is optimized and is equal to the fraction of flow dedicated to reduction. The fuel production rate in the $t_{tot} \rightarrow 0$ limit is independent of material thermodynamics, and when appropriately normalized, to the amount of material. The gas utilization metrics, generically $\bar{U}$, are maximized in the limit in which the relevant $N \rightarrow 0$. Ignoring the trivial case in which $F_{tot} \rightarrow 0$, $N \rightarrow 0$ is attained when $t_{tot} \rightarrow 0$, or when the relevant $\theta \rightarrow 0$. The values of these metrics do not depend on how $N \rightarrow 0$ is achieved, and hence they are independent of cycle time when the relevant $\theta \rightarrow 0$. The gas utilization metrics are fully maximized (generically denoted $\bar{U}^{max}$) when the relative number of moles of gas used in reduction vs. oxidation (ξ_{red}) is optimized. Moreover, both the maximum fuel production rate and the maximum values of the gas utilization metrics are *entirely* independent of material thermodynamics.

Optimization of Fuel Production Rate with Temperature and Gas Composition.

While the maximum fuel production rate, $\bar{Q}^{max}$, and the maximum values of the gas utilization metrics, $\bar{U}^{max}$, are, as just described, independent of material thermodynamics and mass, it is clear on examination of Equation (36) that $\bar{Q}^{max}$ and hence also $\bar{U}^{max}$ depend on the thermodynamic properties of the reducing and oxidizing gases. Accordingly, the next step in the analysis is to evaluate the impact of temperature and gas composition on the fuel production process. For brevity, only the behavior of $\bar{Q}^{max}$ is considered in detail. As mentioned above, the gas flow conditions of $\bar{Q}^{max}$ do not coincide with those of $\bar{U}^{max}$. However, the impacts of changing temperature and gas composition are similar between these terms due to the general relationship $\bar{U} = \bar{Q}/\theta$, as given in Eqs. (45), (57) and (62). In Table 1 is summarized the impact of changing the reduction gas, the oxidation gas and temperature on relevant fuel production quantities. For each combination of conditions, $\bar{Q}^{max}$ is obtained by varying $\Phi^{max}(= f_{red}^{max})$, the value of which is also reported. In addition the values of $\bar{U}_{N_{tot}}$ and $\bar{C}_{H_2O}$ at the conditions of $\bar{Q}^{max}$ are also provided. It is emphasized that all of these values are determined in the $t_{tot} \rightarrow 0$ limit.

Lowering the steam content from 100% to the experimentally more manageable value of 20% has a very large negative effect on $\bar{Q}^{max}$, resulting in a decline of 67%. This behavior is connected to the overall decrease in volume of fuel per unit oxide mass discussed earlier on comparing these two oxidizing conditions. Varying the concentration of oxygen in the reduction gas, in contrast, has a relatively small effect. Even with an order of magnitude increase in oxygen concentration, from 10 to 100 ppm O₂, $\bar{Q}^{max}$ decreases by only 14%. The relative insensitivity of normalized fuel productivity to P_{O_2in} derives from the fact that $\bar{Q}^{max}$ occurs for a cycle in which the material has a relatively high $P_{O_2}(\delta^*, T_0)$, as reported in Table 1. The rate of reduction is proportional to the difference between $P_{O_2}(\delta^*, T_0)$ and P_{O_2in} , Eq. (7), and becomes dominated by $P_{O_2}(\delta^*, T_0)$ when P_{O_2in} is less than 100 ppm O₂. On the one hand, this result implies that the reducing power of the inert sweep gas can be relaxed away from the 10 ppm value used in these calculations, ultimately lowering the parasitic energy penalties and system cost, but on the other hand, it implies that the rate of hydrogen production cannot be improved by changing the composition of the sweep gas (for example, utilizing 1 ppm O₂ instead will have a negligible impact). The temperature of operation has a substantial impact on the characteristic fuel productivity. Increasing the temperature to 1600 °C almost doubles $\bar{Q}^{max}$ and conversely, lowering it to 1400 °C halves it

relative to operation at 1500 °C. This behavior reflects the increase in the extent of the thermolysis reaction with increasing temperature.

The most significant impact on $\bar{Q}^{max}$ arises from changing the oxidation gas from H₂O to CO₂. At these high temperatures, autodissociation of CO₂ proceeds to a far greater extent than that of H₂O. The greater oxidizing power of CO₂ results in a 150% increase in characteristic fuel production over H₂O. This gas composition has been tested experimentally, in which an average CO production rate, as measured over 100 cycles, corresponding to value of $\bar{Q}$ of 5.3×10^{-4} was measured at $f_{red} = 0.39$ and $\Phi = 0.75$, [28] close to the theoretical maximum of 5.9×10^{-4} . This experimentally measured rate is substantially higher than is theoretically possible for oxidation with steam and thus it may be preferable to generate CO rather than H₂ in isothermal, pressure-swing cycling. Oxidation with a mixture of H₂O and CO₂ could also be considered in order to generate a mixture of H₂ and CO (syngas) in the product stream. However, because of the lower oxidizing power of H₂O, this would result in lower overall fuel productivity. Instead, if one aims to create syngas, it would be preferable for the oxidation to be performed with pure CO₂, thereby maximizing fuel productivity, and then to introduce H₂O at a lower temperature, at which equilibration will convert a portion of the CO generated in the first step to H₂.

Optimization of Fuel Production Rate at Finite Cycle Time: Material and Mass.

While the $t_{tot} \rightarrow 0$ limit provides a useful framework for evaluating maximum fuel production rates, operation in this limit is unrealistic in a practical setting. As shown below, operation away from this condition creates an opportunity to optimize the fuel production rate *via* material mass or as previously demonstrated, [31] material choice. The same is not true of the (material-independent) optimized gas utilization metrics. This is because the $\bar{U}^{max}$ values are attained at any value of t_{tot} so long as the rather plausible condition $\theta \rightarrow 0$ is met. Thus, if one modulates the fraction of time and fraction of flow devoted to reduction vs. oxidation to achieve $\theta \rightarrow 0$, there are no further modifications to the process, be it cycle time, material choice, or mass of material, than can be manipulated to impact $\bar{U}$. Accordingly, the subsequent analysis of the impact of cycle time focuses on fuel production rates.

To aid the discussion, we extend the concept of the characteristic hydrogen production rate, $\bar{Q}$, to a form, $Q(\delta)$, that describes the characteristic hydrogen production rate experienced by the material over an *incremental* swing in nonstoichiometry. By analogy to Eq. (33), Q is expressed as

$$Q(\delta) = \frac{\dot{v}_{H_2}^{tot} m_{CeO_2}}{V_M F_{tot}} \quad (64)$$

where $\dot{v}_{H_2}^{tot}$ is the differential form of Eq. (23):

$$\dot{v}_{H_2}^{tot} = \frac{V_M}{M_{CeO_2}} \frac{d\delta}{dt_{tot}} \quad (65)$$

This term expresses the rate of hydrogen production for a complete cycle, in which the cycle time includes that required to reduce the material by $d\delta$ ($= d\delta_{red}$) as well as the time required to oxidize it by $-d\delta$ ($= d\delta_{ox}$), at a nonstoichiometry (in both half-cycles) of δ . Combining Equations (64) and (65) and noting that $d\delta/dt_{tot}$ can be expressed in terms of the components $d\delta_{red}/dt$ and $d\delta_{ox}/dt$ yields

$$Q(\delta) = \frac{n_{CeO_2}}{F_{tot}} \left(\left(\frac{d\delta_{red}}{dt} \right)^{-1} - \left(\frac{d\delta_{ox}}{dt} \right)^{-1} \right)^{-1} \quad (66)$$

As the two rate terms in this expression have already been derived (given in Equations (7) and (20), respectively), the form of $Q(\delta)$ is entirely known.

Physically, $Q(\delta)$ represents the infinitesimal contribution to the characteristic hydrogen production rate, $\bar{Q}$, for any cycle passing through δ . From the expressions for $d\delta_{red}/dt$ and $d\delta_{ox}/dt$ that determine the functional form of Q , it is evident that Q can be defined either as a function of δ , as has been done to this point, or as a function of the equivalent $P_{O_2}(\delta, T_0)$. Indeed, the latter choice is somewhat more intuitive given that $d\delta_{red}/dt$ and $d\delta_{ox}/dt$ depend explicitly on oxygen partial pressure and only implicitly on oxygen nonstoichiometry. Significantly, when expressed in terms of P_{O_2} , Q becomes entirely independent of material properties. That is, although the relationship between P_{O_2} and δ is unique to each material, the relationship between Q and P_{O_2} is not. Of further significance is that Q is independent of the half-cycle times and hence of f_{red} (the fraction of time devoted to reduction) and t_{tot} (the total cycle time). However, because F_{red} and F_{ox} appear, respectively, in $d\delta_{red}/dt$ and $d\delta_{ox}/dt$, Q depends on Φ (the fraction of flow devoted to reduction). A representative result (computed using $\Phi = 0.57$) comparing the two functional forms of Q is presented in Figure 5.

The characteristic hydrogen production rate, $\bar{Q}$, is now recognized as the mean value of Q for a cycle between specified nonstoichiometry values, δ_i and δ_f , or between the limits $P_{O_2}(\delta_i, T)$ and $P_{O_2}(\delta_f, T)$, and can be directly expressed as:

$$\bar{Q} = \frac{\int_{\delta_i}^{\delta_f} Q d\delta}{\Delta\delta} \quad (67)$$

or

$$\bar{Q} = \frac{\int_{P_{O_2}(\delta_i, T)}^{P_{O_2}(\delta_f, T)} Q dP_{O_2}}{\Delta P_{O_2}} \quad (68)$$

where the (f_{red}, t_{tot}) values of the cycle become specified upon selection of δ_i and δ_f . In the limit of $\Delta\delta \rightarrow 0$, equivalent to the $t_{tot} \rightarrow 0$ limit, $\delta_i = \delta_f = \delta^*$ and $\bar{Q}$ will limit to $Q(\delta^*)$, where the particular value of δ^* and hence of $Q(\delta^*)$ will be fixed by the value of f_{red} . Thus, each point on the $Q(\delta)$ curve corresponds to a $\{\bar{Q}, f_{red}\}$ pair relevant to a cycle carried out in the $t_{tot} \rightarrow 0$ limit. The occurrence of a single maximum in Q , as plotted in Figure 5, implies that high productivity cycles carried out away from the $t_{tot} \rightarrow 0$ limit must traverse this peak. Indeed, it can be shown that for a given value of t_{tot} , the value of f_{red} that maximizes $\bar{Q}$, $f_{red}^{opt}(t_{tot})$, occurs when the condition $Q(\delta_i) = Q(\delta_f)$ [or $Q(P_{O_2}(\delta_i, T_0)) = Q(P_{O_2}(\delta_f, T_0))$] holds (see SI), which in turn, requires, by Rolle's theorem, that δ_i and δ_f lie on opposing sides of the peak. Combining the f_{red} optimization with the $t_{tot} \rightarrow 0$ limit, implies that the peak value of Q evident in Figure 5 corresponds to the maximum value of $\bar{Q}$ for the given Φ . Because Φ has been set equal to 0.57 (the optimized value of Φ for the $t_{tot} \rightarrow 0$ limit, Φ^{max}) the peak Q in Figure 5 is equal to $\bar{Q}^{max}$. Again, it is evident that $\bar{Q}^{max}$ is independent of material thermodynamics.

With this backdrop, it is clear why materials with a small magnitude of $dP_{O_2}/d\delta$ ($P_{O_2}^{max}$) are advantageous for fuel production by isothermal cycling.[31] In such materials, a change in δ induces only a small shift in $P_{O_2}(\delta, T)$ away from $P_{O_2}^{max}$ and hence $\bar{Q}$, which depends only on $P_{O_2}(\delta, T)$, will approach $\bar{Q}^{max}$ even for non-zero cycling times. A comparison of several materials are provided in Table S1 (see SI). In the limit $dP_{O_2}/d\delta$ ($P_{O_2}^{max}$) $\rightarrow 0$ one obtains a stoichiometric phase change material. While potentially attractive thermodynamically, the benefits of rapid oxygen diffusion resulting from a high vacancy concentration is typically lost in such systems, suggesting the thermo-kinetic limit discussed here may not be applicable and optimal cycling conditions will be governed by other factors. The properties of $\bar{Q}$ also permit interpretation of the impact of mass on reactor operation. From the factor n_{CeO_2}/F_{tot} in Equation (66) it is clear that mass (through the number of moles) and total flow rate are equally significant and thus that the relevant process parameter is the ratio of mass to total flow rate, rather than mass alone. For ease

of discussion, however, the numerical analysis is performed using a fixed flow rate (specifically, a volumetric flow rate of $\dot{V}_{tot} = 500$ sccm) and the discussion is framed in terms of varied mass rather than a flow rate normalized quantity. In Figure 6 are shown traces of $\bar{Q}$ as a function of t_{tot} while maintaining $f_{red} = f_{red}^{opt}(t_{tot})$ for different masses of material in the reactor (computed with $\Phi = \Phi^{max}$). As expected, at the $t_{tot} \rightarrow 0$ limit, changing mass has no impact on $\bar{Q}$, and increasing t_{tot} causes $\bar{Q}$ to decrease, Figure 6a. Away from the $t_{tot} \rightarrow 0$ limit, $\bar{Q}$ is very sensitive to mass, and it is evident that more mass in the reactor allows $\bar{Q}$ to retain a high value to longer cycle times. As $\bar{Q}$ is proportional to $\bar{v}_{H_2}$, dependence of $\bar{Q}$ on mass requires that, away from the $t_{tot} \rightarrow 0$ limit, $\bar{v}_{H_2}$ deviates from an inverse dependence on mass, behavior that is captured in Figure 6b. Physically, the enhancement of $\bar{Q}$ with increasing oxide mass occurs because, at a given t_{tot} and given oxidation and reduction gas compositions and flow rates, the overall swing in material nonstoichiometry decreases ($\Delta\delta/t_{tot}$ is inversely proportional to oxide mass via Eqs. (7) and (20)). Thus, the material increasingly behaves as it if were in the $t_{tot} \rightarrow 0$ limit.

METHODS. The gas release profiles were computed according to Equations (7) and (20) in a stepwise manner using in-house written MATLAB programs using one of two approaches described previously[31] and repeated here for clarity. In the first, the initial δ for a given half-cycle was taken as a specified input, the slope, $d\delta/dt$, was calculated according to the derived expressions, a new δ was then computed using a time step of 6 ms, and the calculation repeated until δ reached within 10^{-5} of the equilibrium value. A computationally more efficient method involved the determination of $d\delta/dt$ at fixed steps in δ of 10^{-5} , and using the inverse of this value ($= dt/d\delta$) to calculate the time required to reach the next step in δ . The thermodynamic inputs, reduction enthalpy and entropy of ceria as a function of nonstoichiometry, were linearly interpolated from digitized values taken from graphs of data in the literature.[31] The thermodynamic properties of water dissociation were obtained using the HSC Chemistry software.[34]

CONCLUDING REMARKS. We have presented a global optimization of hydrogen production metrics, hydrogen production rate and gas utilization, for pressure-swing thermochemical cycling within the gas-phase limited regime using a thermo-kinetic model. The optimization has been performed varying the cycle times, reduction and oxidation gas flow rates, gas composition, and reactor temperature. It was shown that the maximum characteristic hydrogen

production rate, $\bar{Q}^{max}$, which occurs in the $t_{tot} \rightarrow 0$ limit and at $f_{red} = f_{red}^{max}$, varies only with the gas compositions and the reactor temperature. Reflecting this result, we found that higher fuel productivity can be achieved in converting CO₂ to CO compared to the conversion of H₂O to H₂ due to the higher oxidizing power of CO₂ at typical reactor temperatures (1500 °C) and thus CO production may be preferable to H₂ production in isothermal, pressure-swing cycling. Moreover, rates will monotonically increase with increasing temperature. Finally, we found that $\bar{Q}^{max}$ represents a meaningful fuel production rate limit for a given set of gases and reactor temperature to which experimental results can be compared. The gas utilization metrics, generically $\bar{U}$, were shown to be directly related to $\bar{Q}$. In analogy to the latter, the $\bar{U}$ terms were found to be maximized in the limit $N \rightarrow 0$, where N is the gas input which is to be minimized for a given quantity of fuel production. This limit can be achieved not only when $t_{tot} \rightarrow 0$, but also when $\theta \rightarrow 0$, where θ correlates the relevant flow rate to the total flow rate. Because approaching the $\theta \rightarrow 0$ limit is experimentally plausible depending on the nature of the relevant gas (input steam, for example), we consider it to be the condition that will more likely be employed to give $N \rightarrow 0$. In such case the $\bar{U}$ metrics become independent of cycle time, behavior which is quite distinct from $\bar{Q}$, which monotonically decreases with increasing cycle time. Under finite cycling times, material thermodynamics and mass become important in establishing $\bar{Q}$, providing an opportunity for materials design to enhance fuel productivity.

The relevance of this analysis to real reactors derives from the need to operate at low gas flow rate relative to mass of reactive oxide so as to mitigate against high heat losses from large quantities of reactant gases. Indeed, even in pressure-swing operation, reactor efficiency is dominated by heat recuperation of flow gases. Thus, efficient reactors are expected to operate within the gas-phase limited regime described here. To this end, detailed reactor models, which, as proposed here, treat oxygen stoichiometry changes in the reactive oxide to be limited by gas flow, have very recently appeared in the literature.[33,36,37] The thermo-kinetic model presented here can provide guidance for enhancing fuel production rates for a *generic* reactor design, so long as it obeys the constraints that the material stoichiometry and gas phase composition be spatially uniform in the reaction zone. In particular, we show that although some improvement in rate can be realized by employing reactive materials with improved thermodynamic properties, the production rate is primarily increased by optimizing the gas flow parameters and reactor operation conditions. The material kinetic properties, unless they become extremely degraded in pursuit of enhanced

thermodynamics (which can only, in any case, yield moderate benefit), essentially play no role. Thus, efforts to increase the reaction kinetics by increasing surface area, surface reaction rate or bulk diffusivity are misplaced. Finally, regardless of whether the reactor operates within the gas-phase limited regime, because the thermo-kinetic model considers material kinetics to be infinitely fast, $\bar{Q}^{max}$ and $\bar{U}^{max}$ represent, in some sense, theoretical maximum values.

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NOMENCLATURE.

δ	oxygen nonstoichiometry
δ^*	oxygen nonstoichiometry during an instantaneous cycle
δ^{*opt}	oxygen nonstoichiometry during an instantaneous cycle with $f_{red} = f_{red}^{opt}$
δ_f	oxygen nonstoichiometry at end of the reduction half-cycle
δ_i	oxygen nonstoichiometry at initiation of the reduction half-cycle
$\Delta\delta$	change in oxygen nonstoichiometry over a half-cycle
$\Delta\delta_{ox}$	change in oxygen nonstoichiometry over the oxidation half-cycle
$\Delta\delta_{red}$	change in oxygen nonstoichiometry over the reduction half-cycle
$\Delta\delta/N$	cycle-averaged change in nonstoichiometry per mole of gas (mol^{-1})
$\Delta\delta/t_{tot}$	cycle-averaged rate of change in nonstoichiometry (min^{-1})
$d\delta_{ox}/dt$	rate of change in oxygen nonstoichiometry during the oxidation half-cycle (min^{-1})
$d\delta_{red}/dt$	rate of change in oxygen nonstoichiometry during the reduction half-cycle (min^{-1})
$\theta_{N_{H_2O}}$	total molar flow rate to cycle-averaged molar flow rate of water conversion factor
	$\theta_{N_{H_2O}} = \bar{F}_{H_2O}/F_{tot}$
$\theta_{N_{tot}}$	total molar flow rate to cycle-averaged molar flow rate conversion factor
	$\theta_{N_{tot}} = \bar{F}/F_{tot}$
θ_{N_w}	total molar flow rate to cycle-averaged cost-weighted molar flow rate conversion factor
ξ_{red}	fraction of reduction moles in total moles of gas passed through reactor during one cycle, $\xi_{red} = N_{red}/N_{tot}$

684	ξ_{red}^{max}	ξ_{red} at maximum value of $\bar{U}_{N_{tot}}$ during an instantaneous cycle
685	χ_{H_2O}	mole fraction of water in inlet gas
686	$\dot{v}_{H_2}$	volumetric hydrogen production rate per gram of oxide (sccm g ⁻¹)
687	$\dot{v}_{H_2}^{t_{tot}}$	cycle-averaged volumetric hydrogen production rate for an incremental swing in
688		nonstoichiometry (sccm g ⁻¹)
689	$\bar{\dot{v}}_{H_2}$	cycle-averaged volumetric hydrogen production rate per gram of oxide (sccm g ⁻¹)
690	$\dot{v}_{O_2}$	volumetric oxygen production rate per gram of oxide (sccm g ⁻¹)
691	Φ	reduction flow rate fraction of total flow rate $\Phi = F_{red}/F_{red} + F_{ox}$
692	Φ^{max}	Φ at $\bar{Q}^{max}$
693	ψ	extent of reaction of water
694	$\bar{C}_{H_2O}$	cycle-averaged steam conversion
695	f_{red}	fraction of cycle time allotted to reduction, $f_{red} = t_{red}/t_{red} + t_{ox}$
696	f_{red}^{max}	f_{red} at $\bar{Q}^{max}$
697	f_{red}^{opt}	f_{red} that maximizes hydrogen production rate at a given t_{tot}
698	$\bar{F}$	cycle-averaged molar flow rate, $\bar{F} = N_{tot}/t_{tot}$ (mol min ⁻¹)
699	F_{out}	molar flow rate at outlet of reactor (mol min ⁻¹)
700	F_{ox}	molar flow rate at inlet of reactor during oxidation (mol min ⁻¹)
701	F_{red}	molar flow rate at inlet of reactor during reduction (mol min ⁻¹)
702	F_{tot}	total molar flow rate, $F_{tot} = F_{red} + F_{ox}$ (mol min ⁻¹)
703	F_{H_2Oin}	molar flow rate of water at inlet of reactor (mol min ⁻¹)
704	F_{H_2Oout}	molar flow rate of water at outlet of reactor (mol min ⁻¹)
705	F_{O_2in}	molar flow rate of oxygen at inlet of reactor (mol min ⁻¹)
706	F_{O_2out}	molar flow rate of oxygen at outlet of reactor (mol min ⁻¹)
707	ΔH_{red}	enthalpy of reduction (kJ mol ⁻¹)
708	K_{H_2O,T_0}	equilibrium constant for water thermolysis at temperature T_0
709	M_{CeO_2}	molar mass of ceria (g mol ⁻¹)
710	m_{CeO_2}	mass of ceria (g)
711	N	moles of gas, arbitrary basis (mol)
712	N_{ox}	moles of oxidizing gas passed through reactor during oxidation half-cycle (mol)

713	N_{red}	moles of reducing gas passed through reactor during reduction half-cycle (mol)
714	N_{tot}	moles of gas passed through reactor during one cycle (mol)
715	n_{CeO_2}	moles of ceria (mol)
716	P_{ref}	reference pressure (atm)
717	P_{tot}	total pressure in reactor (atm)
718	$P_{O_2}(\delta, T)$	oxygen partial pressure of a gas in equilibrium with a material at a
719		nonstoichiometry of δ and temperature T (atm)
720	P_{O_2in}	oxygen partial pressure at the reactor inlet (atm)
721	P_{O_2out}	oxygen partial pressure at the reactor outlet (atm)
722	$P_{O_2}^{max}$	$P_{O_2}(\delta, T)$ at $\bar{Q}^{max}$ (atm)
723	r_{O_2}	rate of oxygen generation (or consumption) (mol min ⁻¹)
724	ΔS_{red}	entropy of reduction (J mol ⁻¹ K ⁻¹)
725	T_0	temperature of the reactor (K)
726	t	time (min)
727	t_{ox}	oxidation half-cycle time (min)
728	t_{red}	reduction half-cycle time (min)
729	t_{tot}	total cycle time, $t_{tot} = t_{red} + t_{ox}$ (min)
730	V_M	molar volume (L mol ⁻¹)
731	$\dot{V}_{tot}$	total volumetric flow rate, $\dot{V}_{tot} = V_M F_{tot}$ (sccm)
732	$\bar{U}$	cycle-average gas utilization for an arbitrary molar gas basis, N
733	$\bar{U}_{N_{tot}}$	cycle-averaged total gas utilization
734	$\bar{U}_w$	cycle-averaged cost-weighted gas utilization
735	$\bar{U}^{max}$	maximum $\bar{U}$ for a given set of reducing and oxidizing gases
736	Q	characteristic hydrogen production rate for an incremental change in
737		nonstoichiometry
738	$\bar{Q}$	characteristic hydrogen production rate
739	$\bar{Q}^{max}$	maximum $\bar{Q}$ for a given set of reducing and oxidizing gases
740	w_{ox}	cost weight of oxidation gas
741	w_{red}	cost weight of reduction gas

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TABLES.

Table 1. Maximized characteristic fuel production as a function of flow gas mixture and temperature.

Temperature (°C)	Reduction Gas	Oxidation Gas	$P_{O_2}^{max} \times 10^4$ (atm)	Φ^{max} ($= f_{red}^{max}$) (unitless)	$\bar{Q}^{max} \times 10^4$ (unitless)	$\bar{U}_{N_{tot}} \times 10^4$ (unitless)	$\bar{C}_{H_2O(CO_2)} \times 10^4$ (unitless)
1500	10 ppm O ₂	H ₂ O (100%)	3.8	0.57	2.4	4.8	13.1
1500	10 ppm O ₂	20% H ₂ O	1.3	0.57	0.8	1.6	4.4
1500	1 ppm O ₂	H ₂ O (100%)	3.7	0.58	2.5	4.8	13.3
1500	100 ppm O ₂	H ₂ O (100%)	4.3	0.56	2.1	4.1	11.3
1400	10 ppm O ₂	H ₂ O (100%)	1.9	0.58	1.2	2.4	6.6
1600	10 ppm O ₂	H ₂ O (100%)	6.9	0.57	4.5	8.8	24.2
1500	10 ppm O ₂	CO ₂ (100%)	9.4	0.56	5.9	11.6	32.1

FIGURE CAPTIONS.

Figure 1. Isothermal pressure-swing cycle of ceria at 1500 °C. The equilibrium stoichiometry of ceria at 1500 °C as a function of oxygen partial pressure is represented by the black line.[38] Ceria is first allowed to equilibrate with the oxidation gas, steam, thereby reaching state 1. The gas flow is switched to the reduction gas, 10 ppm O₂ in Ar, and the material is reduced until it reaches equilibrium with the inlet gas at state 2. The flow gas is then switched to the oxidation gas, after which the material is oxidized until it reaches equilibrium with the oxidation inlet gas at 1, completing the cycle. Shorter reaction times produce smaller swings along the non-stoichiometry curve.

1 column

907

a) reduction conditions

b) oxidation conditions

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909 Figure 2. Schematic of the thermochemical reactor under gas-phase limitation: (a) reduction
910 conditions, and (b) oxidation conditions.

911 2 columns

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Figure 3. Variation of the characteristic hydrogen production rate during isothermal pressure swing cycling of ceria at the limit of instantaneous cycle time ($\bar{Q}(t_{tot} \rightarrow 0)$) as a function of the fraction of cycle time allotted for reduction (f_{red}) and of the fraction of flow rate allocated to the reduction flow (Φ) in the thermo-kinetic model (computed for $T = 1500$ °C; ceria mass $m = 0.5$ g; reduction gas of 10 ppm O_2 in Ar; oxidation gas of H_2O ; total volumetric flow rate $\dot{V}_{tot} = 500$ sccm). Results are presented as a surface plot in (a) and as a contour plot in (b).

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Figure 4. Variation of the characteristic hydrogen production rate and steam conversion ration

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during isothermal pressure swing cycling of ceria at the limit of instantaneous cycle time (

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$\bar{U}_{N_{tot}}(N_{tot} \rightarrow 0)$, $\bar{C}_{H_2O}(N_{H_2O} \rightarrow 0)$) in the thermo-kinetic model (computed for $T = 1500$ °C; ceria

937

mass $m = 0.5$ g; reduction gas of 10 ppm O_2 in Ar; oxidation gas of H_2O ; total volumetric flow

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rate $\dot{V}_{tot} = 500$ sccm) as a function of the fraction of cycle time allotted for reduction (f_{red}) and of

the fraction of flow rate allocated to the reduction flow (Φ) (a) and (c), respectively, and as a function of the mole fraction of gas supplied during reduction (ξ_{red}) (b) and (d), respectively.

2 columns

Figure 5. Variation of the incremental characteristic hydrogen production rate, Q , of ceria (a) as a function of δ , and (b) as a function of $P_{O_2}(\delta, T)$.

2 columns

Figure 6. Impact of mass and total cycle time on (a) the characteristic hydrogen production rate $\bar{Q}$ and (b) the average hydrogen production rate, $\bar{v}_{H_2}$, during isothermal pressure swing cycling of ceria. Data points shown with symbols in (b) correspond to the mass values selected in (a). Cycles are calculated with $f_{red} = f_{red}^{opt}(t_{tot})$, $\Phi = \Phi^{max}$ at 1500 °C and $\dot{V}_{tot} = 500$ sccm.

2 columns