Cascading Pressure Thermal Reduction for Efficient Solar Fuel Production

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Abstract

Efficient two-step solar-thermochemical fuel production requires vacuum pumping or inert gas sweeping to lower the oxygen pressure in the thermal reduction step. Pumping is hampered by large oxygen volumetric flows, whereas sweeping is energy-intensive, requiring heat recovery at high temperature, and a dedicated inert gas purification plant. A novel pumping approach—using a cascade of chambers at successively lower pressures—is analyzed and shown to lead to over an order of magnitude pressure decrease compared to a single-chambered design. The resulting efficiency gains are substantial, and represent an important step toward practical and efficient solar fuel production on a large scale.

Keywords: Hydrogen, thermochemical, solar fuels, carbon dioxide

1. Introduction

Two-step thermochemical cycles are a conceptually simple, theoretically highly efficient, and promising approach for solar fuel production. In the first step—thermal reduction—a reactive material (oxide) is partially or fully reduced at high temperature (typically 1600–1800K). In the second step—fuel production—the reduced oxide is exposed to steam or CO₂ at a lower temperature (1100–1500K), to produce H₂ or CO.[1-4]

Efficiencies achieved in experiments have been much lower than theoretical limits, largely owing to the performance of existing reactive oxides. The low reversible oxygen capacity of these oxides results in low H₂ or CO yields per mole oxide per cycle, leading to large energy requirements for oxide heating.[5, 6] Increasing the per-cycle yield has proven to be challenging—requiring high thermal reduction temperatures (T_{TR}) and low thermal reduction pressures (p_{TR}). High temperatures cause excessive aperture radiation losses and require the use of specialized construction materials, limiting T_{TR} to <1800K. Low pressures can be achieved by inert gas sweeping or vacuum pumping—both facing limitations for reasonably-scaled commercial systems (1-10MW). Sweeping requires large amounts of high-purity gasses and extensive high-temperature heat recovery, whereas pumping requires excessively large vacuum pumps, limiting the minimum achievable p_{TR} . [7]

A previously unexplored pumping approach is the use of a *pressure cascade*—i.e. multiple thermal reduction chambers at successively lower pressures—to achieve low p_{TR} . Theoretical aspects, efficiency benefits, and implementation modes and limits of a pressure cascade, are examined in this paper. The results indicate a potential for a significant p_{TR} limit decrease and efficiency gains in two-step thermochemical cycles.

2. Thermochemical cycles: vacuum pumping advantages and limitations

Reactions (1) and (2) below, generically describe a two-step thermochemical cycle for H₂ production, based on a reactive metal oxide (MO_x). Reaction (1) is an endothermic thermal reduction of the oxide carried out at a temperature T_{TR} . Reaction (2) is the mildly exothermic reoxidation of the reduced oxide with H₂O, at temperature T_{WS} , which yields H₂ and restores the

oxide to its initial state. The process can also be used to produce CO from CO₂ in reaction (2). The sum of the two reactions is heat-driven H₂O splitting, described by reaction (3):

Here, δ_{TR} and δ_{WS} are the extents of reduction of the oxide following the thermal reduction and water splitting steps. Low p_{TR} (or, more generally, p_{O_2}) in reaction (1) increases δ_{TR} and the reversible oxygen capacity $\Delta\delta = \delta_{TR} - \delta_{WS}$. Because the H₂ yield per mole oxide per cycle is proportional to $\Delta\delta$, lowering p_{TR} generally increases efficiency.[7-12]

Achieving low p_{TR} , however advantageous, is challenging. The main difficulty are large O₂ volumetric flows—not pumping work, O₂ mass flow, or aerodynamic loads.[7] Indeed, a 1MW chemical output corresponds to ~3.5mol/s H₂ and an O₂ mass flow rate of only ~55 g/s. Nonetheless, at low pressure, even modest mass flow rates require pumping at large volumetric rates, $\dot{V}_{O_2}$, and at high O₂ flow velocities, $v_{O_2} = \dot{V}_{O_2}/A_{ox}$.

To quantify v_{O_2} and $\dot{V}_{O_2}$, consider the surface area of the oxide receiver (A_{ox}), illustrated in the inset in Fig.1a:

$$A_{ox} = A_{coll} / C_B \quad (4).$$

Here A_{coll} is the solar collector/concentrator area (e.g. gross heliostat area) and C_B is the concentration ratio at the oxide receiver (roughly 10% of the concentration ratio at the aperture, C_A). The chemical output power, P , of a H₂-producing reactor, can be expressed in two ways:

$$P = \eta A_{coll} \dot{Q}_S \quad \text{and} \quad P = \dot{n}_{H_2} HHV_{H_2} \quad (5) \text{ and } (6).$$

Here η is the reactor solar-to-hydrogen efficiency, $\dot{Q}_S = 1\text{kW/m}^2$ is the incoming solar flux, $\dot{n}_{H_2}$ is the molar H₂ production rate, and $HHV_{H_2} = 286\text{kJ/mol}$ is the H₂ higher heating value. Combining eqs. (4), (5), (6), and the ideal gas equation, the required v_{O_2} can be expressed as:

$$v_{O_2} = \frac{\eta C_B RT_{TR}}{2 * HHV_{H_2}} \frac{\dot{Q}_S}{p_{TR}} \quad (7).$$

Fig.1a shows v_{O_2} as function of p_{TR} , calculated using eq.(7). While v_{O_2} is quite reasonable for $p_{TR} \approx 100\text{Pa}$ and higher, it reaches hypersonic and even orbital velocity below 1Pa. For lower values of C_B —within a reasonable range— v_{O_2} would be somewhat lower than in Fig.1a, but still excessive at low p_{TR} .

Assuming a maximum $v_{O_2} \approx 100\text{m/s}$, the lowest feasible p_{TR} is around 20Pa—illustrating the limits of pumping. Somewhat higher v_{O_2} values could be considered, but with caution regarding practical flow impediments, such as conductance losses in pumping elements and decreased conductance under molecular flow dynamics at low pressures ($p_{TR} \lesssim 1\text{Pa}$). The speed of sound in O₂ ($c \approx 800\text{ m/s}$ at 1773K) is an upper practical limit under all circumstances.

To calculate $\dot{V}_{O_2}$, a normalization with respect to input solar power (P_S) is needed. From $C_B=300$ follows $A_{ox} \approx 3.33 \text{ m}^2/\text{MW}$, corresponding to $\dot{V}_{O_2}(1 \text{ Pa}) \approx \frac{6450 \text{ m}^3}{s} / \text{MW}$ at $\eta=25\%$. This impractically large value further underscores the challenges of vacuum pumping. To illustrate the advantages of low p_{TR} , an efficiency map of a generic ceria-based water-splitting reactor is shown in Fig.1b.

Figure 1. (a) Required oxygen flow velocity from an oxide receiver as function of p_{TR} , $v_{O_2}(p_{TR}, T_{TR} = 1773 \text{ K})$, for solar-to-hydrogen efficiency between 5% and 25%. One volumetric flow value— $\dot{V}_{O_2}(1 \text{ Pa}) \approx \frac{6450 \text{ m}^3}{s} / \text{MW}$ —is shown as an example. The lower left inset illustrates flow velocity: sunlight from a concentrator (e.g. a heliostat field) enters an aperture (with area A_A) and illuminates an oxide receiver. Oxygen leaves the oxide at v_{O_2} . A high concentration ($C_A \approx 3000$) was assumed, necessary because of the high T_{TR} . $C_B=300$ (b) Efficiency map for a ceria-based reactor at the same T_{TR} , illustrating the efficiency advantage of operating under low p_{TR} . [12]

3. Pressure cascade: efficiency advantages and implementation aspects

An alternative approach—aimed at decreasing $\dot{V}_{O_2}$ and enabling lower p_{TR} limits—consists of performing the thermal reduction step in multiple chambers, each operating at a successively lower pressure. In the cascade concept—illustrated in Fig.2— O_2 is pumped near the pressure at which it evolves from the oxide, with *only a fraction* pumped at the final p_{TR} . In the case of a single thermal reduction chamber (previous section), *all* of the evolved O_2 is pumped at the same lowest system pressure.

To estimate p_{TR} limits, a cascade of identically-sized chambers is assumed ($A_{ox,i} = A_{ox}$), though A_a and C_B may differ between chambers. Because using the highest practically achievable v_{O_2} (or $\dot{V}_{O_2}$) leads to the lowest final p_{TR} , a chamber-independent v_{O_2} is also assumed ($v_{O_2,i} = v_{O_2}$). From these two assumptions follows $\dot{V}_{O_2,i} = \dot{V}_{O_2}$. Lastly, the amount of evolved oxygen depends on the extent of reduction, $\delta_{TR}(p_{TR}, T_{TR})$ —a property of the oxide itself.

Under the above assumptions, the pressure in the i^{th} chamber, $p_{TR,i}$, in which the extent of reduction is $\delta_{TR,i} = \delta_{TR}(p_{TR,i})$, is given by a recursive relationship:

$$p_{TR,i} = \dot{n}_{ox} R T_{TR} \frac{\delta_{TR,i} - \delta_{TR,i-1}}{2 \dot{V}_{O_2}} \quad (8),$$

which is simply the ideal gas equation, with the oxygen quantity determined by an oxide molar flow rate $\dot{n}_{ox}$, and an incremental extent of reduction, $\delta_{inc,i} = \delta_{TR,i} - \delta_{TR,i-1}$. For the first

chamber (labelled “0”) $p_{TR} = p_{TR,0}$ and $\delta_{TR,-1} = \delta_{WS}$. Being a well-characterized candidate material for solar-thermochemical fuel production, CeO_2 is assumed as the reactive oxide.[13, 14] Because $\delta(p_{TR}, T_{TR})$ for CeO_2 follows a complicated relationship, $p_{TR,i}$ is determined numerically for several values of $p_{TR,0}$, in a relevant pressure range. The results of the calculations are shown in Fig.2.

Figure 2. Pumping advantage of a multi-chambered approach. The plot shows the pressure ratio between the 0th and ith chamber for a ceria-based thermochemical reactor. A simple schematic illustration of a cascading pressure reactor, e.g. associated with a tower-heliostat system, is also shown. Assuming that pressure separation between chambers is accomplished by a reactive oxide in packed particle bed form, isolation valves between chambers were deliberately omitted as reactor components.

The potential for p_{TR} improvement in a cascade is excellent—an *order of magnitude* p_{TR} decrease can be achieved in as few as five chambers, compared to a single-chambered reactor (Fig.2). The linear and near-identical $p_{TR,0}/p_{TR,i}$ relationship for all considered values of $p_{TR,0}$ is particular to ceria. Other materials should be expected to exhibit a different $p_{TR,0}/p_{TR,i}$ dependence. A 10-fold p_{TR} decrease corresponds to a roughly 7% absolute solar efficiency increase (Fig.1b).

Since the use of multiple chambers is beneficial, it may seem appealing to assume that arbitrarily many can be used. For example, starting with $p_{TR,0}=40\text{Pa}$, and extending the trend in Fig.2 to 50 chambers, leads to $p_{TR,50}\approx 0.35\text{Pa}$ —a tempting value from an efficiency perspective! However—because $p_{TR,i}\sim\delta_{inc,i}$ (eq. 8)—in every subsequent chamber $\delta_{inc,i}$ decreases, thus limiting number of chambers in practice.

One limit follows from the power per chamber (P_i): in an approximation in which the enthalpy of oxide reduction, ΔH , is independent of or weakly dependent on δ , a decreasing $\delta_{inc,i}$ means a decreasing $P_i\sim\delta_{inc,i}$. For example, assuming that heating between T_{WS} and T_{TR} is accomplished prior to thermal reduction, and that the solar input power in the 0th chamber is $P_0=3\text{MW}$ (used entirely for thermal reduction), then P_5 would be a reasonable 235kW, but P_{50} would be only 26kW. Delivering such low power to into a chamber through a finite aperture (at

$C_A \approx 3000$) would be challenging in a tower-heliostat configuration, even if mitigation methods are devised.

The finite angular diameter of the Sun ($\phi \approx 9 \text{ mrad}$) and windowed-aperture size limits ($A_A \approx 1 \text{ m}^2$), for example, limit the heliostat-aperture distance to $\approx 110 \text{ m}$, constraining tower heights and heliostat field sizes. Costs associated with a large number of chambers, each additional one bringing a diminishing efficiency benefit, should also be considered.

Irrespective of limitations, the above results indicate that at least a 10 to 20-fold p_{TR} decrease can be achieved in a pressure cascade—bringing the minimum practical p_{TR} to 1 Pa or less. Under realistic operating circumstances, the resulting δ_{TR} increase can lead to a substantial efficiency advantage compared to equivalent single-chambered designs (Fig. 1b).

To maintain a pressure difference between neighboring chambers, oxygen flow between them must be negligible. This requirement means that the flow between the i^{th} and the preceding chamber, at pressures $p_{TR,i}$ and $p_{TR,i-1}$, should be $\dot{V}_{i,i-1} \ll \dot{V}_{O_2}$.

One possible approach, placing “airlocks” between chambers, i.e. double valves that open asynchronously, would allow a quasi-continuous oxide flow and reactor operation, while restricting oxygen cross-flow. Unfortunately, airlocks are unlikely to be viable pressure separation devices in the hostile operating environment of solar-thermochemical reactors.

A more practical pressure separation method is one in which the reactive oxide is in the form of a moving packed bed, building on reactor the design described in [7]. In this design, the oxide bed itself acts as a pressure separation agent between chambers, owing to the low gas permeability of packed particle beds, governed by Darcy’s law. Compared to free Hagen–Poiseuille flow, the flow restriction factor depends on the bed permeability, and is $>10^6$ under conditions expected in a reactor for thermochemical fuel production.[15]

In this approach, pressure separation between two chambers can be quantified via the volumetric flow through a packed bed:

$$\dot{V}_{i,i-1} = \frac{k A \Delta p_{TR,i}}{\mu L} \quad (9).$$

Here, $k \approx 10^{-11} \text{ m}^2$ is the bed permeability (typical for fine to medium-sized particulate materials), and $\mu \approx 10^{-4} \text{ Pa s}$ is the gas dynamic viscosity. For a typical $p_{TR,0} < 100 \text{ Pa}$, the pressure difference between chambers can be taken as $\Delta p_{TR,i} \approx 25 \text{ Pa}$. $L \approx 1 \text{ m}$ and $A \approx 100 \text{ cm}^2$ are the length and cross-section area of a connection between chambers.

Under these assumptions, $\dot{V}_{i,i-1} \approx 3 \times 10^{-8} \text{ m}^3/\text{s}$ —a value vastly smaller than the expected $\dot{V}_{O_2} \approx \frac{100 \text{ m}^3}{\text{s}}/\text{MW}$ (power normalization with respect to P_S). This exceptional flow restriction means that oxygen exchange between chambers would effectively consist only of the gas in the bed void fraction ($\dot{V}_{\text{void}}$), itself proportional to the oxide volumetric flow $\dot{V}_{OX}$. For a well-performing oxide ($\Delta\delta \approx 0.2$) with a reasonable molar mass ($M_{ox} \approx 0.2 \text{ kg/mol}$), a bed density ($\rho = 4000 \text{ kg/m}^3$), and a void fraction $\phi = 50\%$, $\dot{V}_{\text{void}} = \frac{\dot{n}_{H_2} M_{OX} \phi}{\rho \Delta\delta} \approx \frac{10^{-4} \text{ m}^3}{\text{s}}/\text{MW}$ —also vastly smaller than $\dot{V}_{O_2}$. These results give confidence that pressure separation between chambers in a cascade can be accomplished under all imaginable practical circumstances, including a wide range of particle sizes.

Conclusions

Large required O_2 volumetric flows and velocities limit the lowest practical achievable pressure in the thermal reduction step of vacuum-pumped, two-step thermochemical cycles for

solar fuel production. These limits can be substantially mitigated by the use of a cascade of thermal reduction chambers, each operating at a successively lower pressure. A reactor design based on a moving packed bed of reactive oxide particles can accomplish the necessary pressure separation between thermal reduction chambers without requiring the use of high-temperature airlocks. The cascade approach has the potential to decrease the thermal reduction pressure limit by over an order of magnitude, to below 1Pa, yielding significant efficiency gains.

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