Thermodynamics of CeO_2 thermochemical fuel production

B. Bulfin*, F. Call, M. Lange, O. Lübben, C. Sattler, R. Pitz-Paal, I. V. Shvets

Abstract

In this work the thermodynamics of thermochemical fuel production using a CeO_2 redox cycle are studied. The need to reduce the oxygen partial pressure in order to improve efficiency is investigated, with both sweep gas and vacuum pumping considered as methods of achieving this. At ambient pressure the cycles can be maximised with respect to the temperature swing, the minimum oxygen partial pressure and the extent of the oxidation reaction. For reduction at 1500 °C the maximum efficiency was found to be 4.5%, which is significantly lower than the values found in previous studies. In addition isothermal operation had very low efficiency (less than 2%) under all of the conditions considered. If the system is operated at lower than ambient pressure, the pumping efficiency will depend on the pressure. From an investigation of commercially available pumps the pressure dependence was given an analytical expression. The results showed the cycles have an optimal operating pressure, and that using sweep gas as well as pumping, only reduced the overall efficiency. The efficiency was maximised with respect to the temperature swing, the reduction pressure and the extent of oxidation, giving a peak efficiency of 7.5% for a reduction temperature of 1500 °C. Reducing the pressure during reduction could also be beneficial due to improved reaction kinetics at lower pressure, and an increased yield due to lower oxygen partial pressures. Recovering heat from both the high temperature ceria and the oxidation reaction, and using it as process heat was also considered. With 60% of this heat being recovered, the peak efficiency for the 1500 °C pumped cycle increased to 11%. Finally the practicality of the cycles, in terms of the quantity of ceria required to maintain continuous operation, are considered and some suggestions for improving the cycle are given.

Keywords: Cerium dioxide, Redox, Energy conversion, Thermochemical cycle, Efficiency

1. Introduction

In recent months, climate change has made many news headlines, largely due to the publication of a three part report which provided a review of scientific bases, impacts and vulnerability, and possible mitigation plans for climate change [1, 2, 3]. It was commissioned by the United Nations, put together by the Intergovernmental Panel on Climate Change, and was the fifth report of its kind. It was based on some 12,000 peer reviewed publications. Although often sensationalized by the media and policy makers, it presents strong evidence that there will be some serious implications for society as a result of climate change.

A major contribution to climate change is the increase of atmospheric CO_2 produced when fossil fuels are combusted. Scientific efforts to reduce the worlds economic reliance upon fossil fuels are on-going and widespread. One area which must be addressed is the large reliance on dense liquid based fuels (petroleum) in many industries such as transportation of goods and people. These fuels are for the most part derived from fossil fuels. Many areas of research aim to tackle this, from the great improvements made in electrical energy storage [4], to the production of synthetic fuels [5], and the proposed hydrogen economy [6]. In this work, a thermodynamic analysis for the production of fuel using ceria is presented with the aim of predicting possible fuel conversion efficiencies and the optimal cycle properties.

Thermochemcial cycles producing fuel driven by either nuclear or renewable sources are numerous [7, 8, 9, 10, 11]. This work is focused on ceria as it is a good benchmark material for use in a two step thermochemical fuel production cycle. It can be partially reduced at high temperatures, releasing some of its oxygen [12, 13]. Remarkably, during reduction, ceria remains in the fluorite phase up until approximatly 17% of the oxygen has been removed [14, 15]. The fact that there is no phase change means that ceria reduction and oxidation offers a very practical and achievable thermochemical cycle [16]. The reduced ceria can then be used to produce fuel by splitting H_2O and CO_2 producing H_2 and CO [17, 18]. These products form syngas which can be refined into denser liquid fuels using the Fischer-Tropsch process [19, 20]. A schematic of this idea is shown in figure 1 with the energy required being supplied by concentrated solar power.

A number of reactor designs for such fuel conversion have been proposed [21, 22, 23, 24], and some prototypes have been constructed and tested [25, 17, 16, 26]. So far, fuel conversion efficiencies have been very low, with values typically in the region of or less than 1 %. Thermodynamic studies of such cycles suggest that solar to fuel efficiencies approaching 30 % could be achievable [27, 28].

The majority of work performed on ceria has been for temperature swing cycles. However, some recent studies have brought to light the possibility of an isothermal cycle [29, 30, 31, 32]. An isothermal fuel production cycle based on ceria has been demonstrated at the laboratory scale by Venstrom *et al.*

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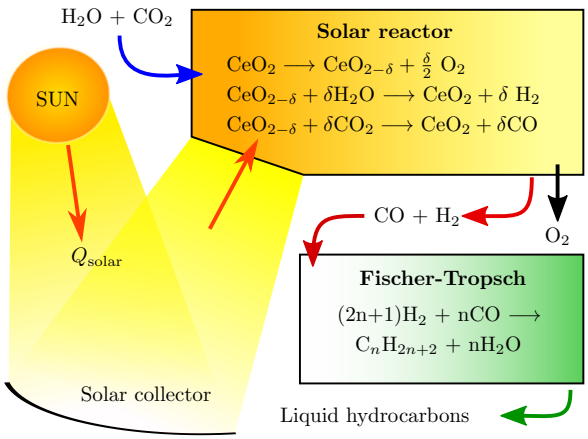

Figure 1: A schematic showing the conversion of H_2O and CO_2 into liquid Hydrocarbons using solar power to drive the ceria redox cycle followed by the conversion of syngas to liquid hydrocarbons via the Fischer-Tropsch process.

[33].

A recent thermodynamic study by Ermanoski *et al.* suggested that isothermal fuel production would have low efficiency due to the unfavorable thermodynamics of an isothermal cycle [34]. They explain that the oxidation and reduction reactions do not proceed spontaneously and without some additional work the yields will be reduced. Instead, the authors determine that there must be a temperature difference between oxidation and reduction which offers a maximum efficiency. This maximum arises because there is a trade off between energy losses due to cycling the temperature and the losses due to operating the cycle under unfavourable thermodynamic conditions.

In this work we provide an analysis of the efficiency of such cycles with a realistic look at the different constraints affecting the efficiency. This includes an analysis on different methods used to reduce the oxygen partial pressure during reduction and a full analysis of the oxidation reaction. This allows the efficiency to be maximised by selecting the cycle parameters.

The oxygen partial pressure can be reduced using a sweep gas with low oxygen concentration (e.g. N_2), by pumping the system to a lower operating pressure during reduction or by some combination of these two methods. The minimum quantities of sweep gas required are calculated using equilibrium considerations.

The pumping efficiency is given a pressure dependence, which has not been considered in previous studies. The lower the operating pressure of the reactor, the less efficient the pumps will be. This is due to pump leakage which increases with decreasing pressure, and thermal losses which increase with the compression ratio. In addition smart pumping (in which oxygen is pumped off at its equilibrium pressure) is used to minimise the energy needed for pumping. This idea was recently highlighted by Ermanoski, who considered the effect of performing reduction in a series of chambers each with decreasing pressure [35], which increased the efficiency.

The oxidation reaction is also given full consideration with the amount of oxidiser needed determined from equilibrium considerations. In some previous cases this quantity may have been underestimated. Here we also introduce a fraction completed parameter to allow the oxidation to stop short of completion which can greatly reduce the amount of oxidiser required.

Finally the practicality of the cycle is discussed based on the amount of ceria which must be used in a reactor per kW of power stored as fuel. These considerations depend on the cycle time (reaction kinetics) and the yield of the cycle.

Nomenclature

δ Oxygen stoichiometry

ΔH_{rd} Change in enthalpy for reduction

T_{rd} Reduction temperature

T_{ox} Oxidation temperature

T_{amb} Ambient temperature

ΔT $T_{rd} - T_{ox}$

δ_{rd} Reduced stoichiometry

δ_{ox} Oxidised stoichiometry

$\Delta\delta_{eq}$ Equilibrium yield

P_{O_2} Oxygen partial pressure

P_{fO_2} Final P_{O_2} during reduction

α Fraction completed for oxidation reaction

C_p Specific heat capcity

ε Heat exchanger effectiveness

n_i Moles of component i

m_i Mass of component i

η_i Efficiency of process i

C Solar concentration

Q_{rd} Energy consumed by reduction

Q_{CeO_2} Energy used to heat ceria

Q_{N_2} Energy required to produce nitrogen

Q_{gas} Energy required to heat the sweep gas

Q_{pmp} Energy required to pump gases

Q_{H_2O} Energy required to heat oxidiser

Q_{ox} Energy released by oxidation reaction

Q_{rec} Recovered process heat

$\dot{Q}_{out}$ Output power

$M(CeO_2)$ Molar mass of ceria

t_{cyc} Cycle time

2. Thermodynamics

All of the thermodynamic properties used in this study have an analytical form, meaning that the calculations can be reproduced with basic mathematical software. The aim of this is to allow other authors to easily modify the calculations to determine the maximum thermodynamic efficiencies for specific reactor properties.

It is also important to note that the analytical functions given require the temperature to be in Kelvin and the pressure to be in bar. However, the plots and the descriptions give the temperature in terms of Celsius for the convenience of the reader.

In the case of a temperature swing cycle, there are inevitably difficulties in recuperating the heat used to change the temperature of the ceria and reusing it in the cycle. There have been some ideas for solid state heat recuperation within the cycle. A counter rotating ring design was proposed by Sandia National Laboratories [36, 37], which allows the relatively hot ceria coming from the reduction zone to transfer heat to the relatively cool ceria coming from the oxidation zone. A similar design was proposed by Lapp *et al.* which used counter rotating concentric cylinders [38]. Unfortunately, the implementation of these designs would greatly increase the reactor complexity and likely introduce unnecessary thermal losses. For this reason it is initially assumed that the solid state change in temperature of the ceria is lost heat.

$$\mathrm{CeO}_{2-\delta_{\mathrm{ox}}} \xrightarrow{heat = \Delta H_{\mathrm{rd}}} \mathrm{CeO}_{2-\delta_{\mathrm{rd}}} + \frac{\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}}}{2}\mathrm{O}_2 \qquad T_{\mathrm{rd}} \tag{1}$$

$$\mathrm{CeO}_{2-\delta_{\mathrm{rd}}} + (\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}})\mathrm{H_2O} \longrightarrow \mathrm{CeO}_{2-\delta_{\mathrm{ox}}} + (\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}})\mathrm{H_2} \qquad T_{\mathrm{ox}} \tag{2}$$

$$\Delta T = T_{\mathrm{rd}} - T_{\mathrm{ox}} \qquad \Delta\delta_{\mathrm{eq}} = \delta_{\mathrm{rd}} - \delta_{\mathrm{ox}} \tag{3}$$

The cycle reactions are described by equations 1 and 2. The ceria is reduced at a temperature T_{rd} in a low oxygen atmosphere with an oxygen partial pressure of P_{fO_2}, to a vacancy concentration of δ_{rd}. It is oxidised at a temperature T_{ox} in a 1 bar steam atmosphere (H_2O) to a vacancy concentration δ_{ox}. Only cycles for which $T_{\mathrm{rd}} \geq T_{\mathrm{ox}}$ are considered, and thus the temperature difference ΔT is always positive or zero ($\Delta T \geq 0$). The equilibrium yield per cycle is the difference in the vacancy stoichiometry $\Delta\delta_{\mathrm{eq}}$. For convenience, the deviations from stoichiometry δ, is defined as a unit-less oxygen vacancy concentration

$$\delta = \frac{[\mathrm{O_{vac}}]}{[\mathrm{Ce}]}, \tag{4}$$

where $[\mathrm{O_{vac}}]$ is the concentration of oxygen vacancies and [Ce] is the concentration of cerium atoms.

The values for equilibrium vacancy concentrations δ can be obtained from the equilibrium equation described in previous work performed by the authors[39], which agrees well with equilibrium values from the literature [12, 14, 40, 41, 42, 43].

$$\left(\frac{\delta}{0.35 - \delta}\right) = 8700 \times P_{\mathrm{O_2}}^{-0.217} \exp\left(\frac{-195.6\ [kJmol^{-1}]}{RT}\right) \tag{5}$$

Here the temperature must be given in Kelvin and the oxygen partial pressure in bar. Re-arranging this equation yields an expression for δ which depends only on temperature and oxygen partial pressure, $\delta(T, P_{\mathrm{O_2}})$. In order to calculate δ_{rd}, both T_{rd} and the final oxygen partial pressure P_{fO_2} are substituted into equation 5. The final oxygen partial pressure P_{fO_2}, is the target lower partial pressure to be attained at the end of the reduction cycle.

In order to calculate δ_{ox}, T_{ox} and the oxygen partial pressure in 1 bar of H_2O at T_{ox} are substituted into equation 5. A similar calculation for CO_2 gives lower values of δ_{ox}, which is more favourable in terms of yield. The values of $P_{\mathrm{O_2}}$ in 1 bar of H_2O or CO_2 were calculated using standard equilibrium conditions, and are given in the supporting information.

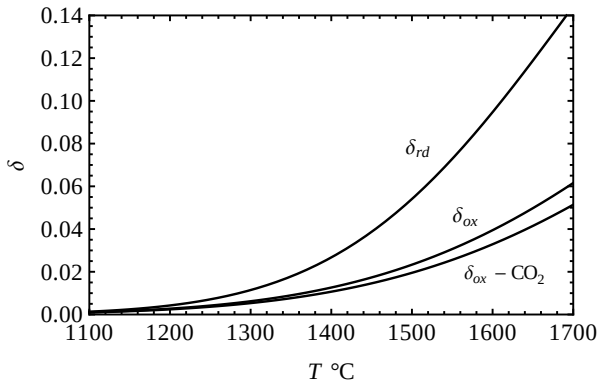

Figure 2: The equilibrium stoichiometry δ vs. the temperature T for a reduction with $P_{fO_2} = 1\times10^{-5}$ bar labelled δ_{rd}, an atmosphere of 1 bar H_2O labelled δ_{ox}, and an atmosphere of 1 bar CO_2 labelled δ_{ox} - CO_2.

H_2O

Figure 2 shows the values of equilibrium δ in a low oxygen partial pressure atmosphere, a steam atmosphere and a CO_2 atmosphere. An isothermal cycle will have a change in stoichiometry equal to the difference between the reduction and oxidation values for a given temperature. The values of δ_{red} and δ_{ox} here agree well with the previous thermodynamic analysis of Bader *et al.* [30].

2.1. Reduction and heating

The energy required to remove oxygen from ceria is the change in enthalpy for reduction, ΔH_{rd}. This change in enthalpy was found by Panlener *et al.* to only depend on the stoicheometry δ [12]. The curve for the change in enthalpy given in Panlener's work was extracted and fit with a polynomial.

$$\Delta H_{\mathrm{rd}}(\delta) = (478 - 1158\ \delta + 1790\ \delta^2 + 23368\ \delta^3 - 64929\ \delta^4)\times10^3 \quad [\mathrm{J\,mol^{-1}}] \tag{6}$$

The heat required to reduce one mole of ceria from δ_{ox} to δ_{rd} can then be calculated by integrating the molar change in enthalpy from δ_{ox} to δ_{rd}. However, oxidising the ceria to δ_{ox} requires that the ceria oxidation reaction reaches equilibrium, which will require excessive amounts of oxidiser. Therefore, it is useful to introduce a stopping point for the oxidation reaction,

$$\delta_{\mathrm{ox}}(\alpha) = \delta_{\mathrm{ox}} + (1 - \alpha)\Delta\delta_{\mathrm{eq}}, \qquad 0 < \alpha \leq 1, \tag{7}$$

where α is the completed fraction of the oxidation reaction. Setting α to values less than one stops the oxidation reaction short of equilibrium. The energy required to reduce a mole of ceria is then

$$Q_{\mathrm{rd}} = \int_{\delta_{\mathrm{ox}}(\alpha)}^{\delta_{\mathrm{rd}}} \Delta H_{\mathrm{rd}}(\delta) d\delta \quad [\mathrm{J\,mol^{-1}}]. \tag{8}$$

For a given cycle, as described previously, there is also the energy cost of heating the ceria. This is given by

$$Q_{\mathrm{CeO_2}} = \int_{T_{\mathrm{ox}}}^{T_{\mathrm{rd}}} C_{p_{\mathrm{CeO_2}}}(T) dT \quad [\mathrm{J\,mol^{-1}}], \tag{9}$$

where the specific heat capacity of ceria was obtained from the work of Pankratz [44], and fit with a polynomial (see supporting material) in the range 300 - 2300 K. The dependence on δ was ignored as within the ranges of δ considered (0 - 0.1), only a 1.5 % change in heat capacity is predicted [14].

The heating efficiency can now be defined as

$$\eta_{\mathrm{heat}} = \frac{\alpha \Delta\delta_{\mathrm{eq}} \mathrm{HHV_{H_2}}}{Q_{\mathrm{rd}} + Q_{\mathrm{CeO_2}}}, \tag{10}$$

where $\alpha\Delta\delta_{\mathrm{eq}}\mathrm{HHV_{H_2}}$ is the energy stored in the fuel, and $Q_{\mathrm{rd}} + Q_{\mathrm{CeO_2}}$ is the heat required to reduce and change the temperature of the ceria. These are the heat inputs to the main part of the reactor as seen in figure 5. The heating efficiency should clearly show the energy losses due to the difference in enthalpies ($\Delta H_{\mathrm{rd}} - \mathrm{HHV_{H_2}}$) and the energy required to cycle the temperature. It sets an upper bound on the fuel production efficiency when there is no solid state heat recovery.

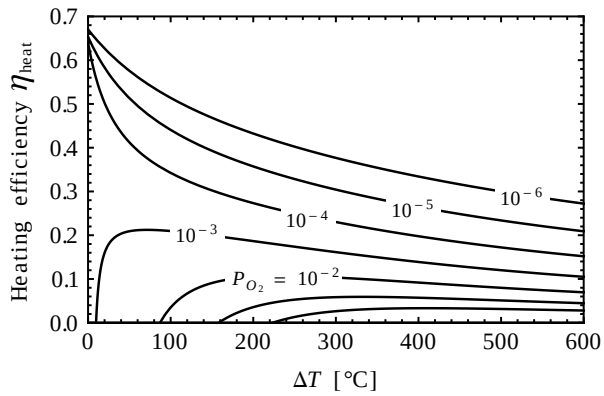

Figure 3: Heating efficiency vs. the change in temperature ΔT for a range of values of P_{fO_2} (1 to 10^{-6} bar), with T_{rd} = 1500 °C and α = 1.

In figure 3 the heating efficiency is plotted for a range of different P_{fO_2}, with T_{rd} = 1500 °C, which is taken as the standard reduction temperature throughout the rest of the manuscript. For the values of $P_{fO_2} > 10^{-4}$ bar, the heating efficiency becomes negative for small ΔT. This is because the cycle is no longer possible as $\Delta\delta_{\mathrm{eq}} < 0$. Otherwise, the heating efficiency again increases with decreasing ΔT and P_{fO_2}. The ceria cycle could be operated with reduction in pure oxygen at ambient pressure, shown by the lowest line in the graph (P_{fO_2} = 1 bar), but the heating efficiency, and thus the fuel production efficiency, is very low (≈ 3 % for ΔT = 500 °C). This shows the importance of reducing the oxygen partial pressure during reduction.

Another very important aspect is the yield, $\Delta\delta_{\mathrm{eq}}$. The number of moles of ceria that need to be heated per cycle to produce 1 mole of H_2 is the inverse of the yield, $\frac{1}{\Delta\delta_{\mathrm{eq}}}$. The thermal losses due to heating of the ceria (re-radiation, insulation losses, etc) will increase if more ceria must be heated to produce a mole of fuel. For this reason cycles with a larger yield should result in less thermal losses per unit of fuel produced. In addition, the practical challenges associated with cycling large amounts of ceria may ultimately decide the technical viability of such cycles.

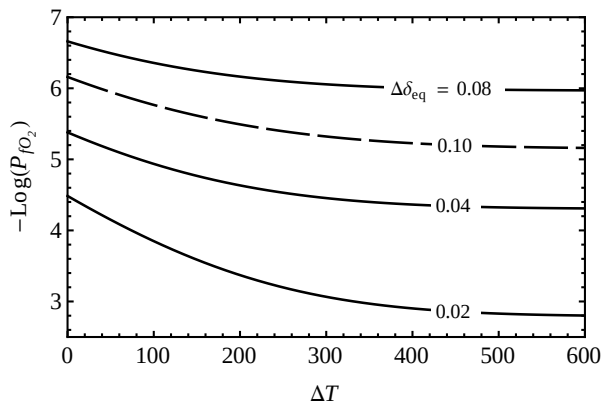

Figure 4: Contours of constant $\Delta\delta_{\mathrm{eq}}$ in a plot of P_{fO_2} vs. ΔT with T_{rd} = 1500 °C. The dashed line is for T_{rd} = 1600 °C.

In figure 4 lines of constant yield are plotted to show the effects of both P_{fO_2} and ΔT on the yield. Increasing ΔT allows for much higher P_{fO_2}, which is important due to the difficulties associated with achieving such low oxygen partial pressures. The dashed line shows the effect of increasing T_{rd} to 1600 °C, which greatly reduces the constraints on ΔT and P_{fO_2} for a given yield. For T_{rd} = 1500 °C the dashed line would be outside the area of the graph at virtually unachievable partial pressures.

The yields shown above are still relatively low and will result in large amounts of ceria being cycled to produce relatively small amounts of fuel. A cycle with T_{rd} = 1500 °C, ΔT = 500 °C and oxygen partial pressures of 10^{-4}, 10^{-5} and 10^{-6} bar will require 29, 19 and 12 moles of ceria (4.8, 3.2 and 2 kg) respectively per mole of fuel produced (2 g). In the worst case of $P_{fO_2} = 10^{-4}$ bar, a reactor with an output of 100 kW would then need to cycle ceria at a rate of 100 kg min^{-1}. If it takes on the order of tens of minutes to complete one full cycle then a 100 kW reactor would need a number of tons of ceria to operate continuously.

Although rough, these considerations highlight the importance of the yield of the cycle and the rate of cycling (reaction kinetics). These parameters determine the amount of ceria a reactor will require which will greatly affect the practicality of the cycle. These properties are given further consideration

in the discussion section, and for now the focus shall return to efficiency.

2.2. Sweep gas

During the reduction step the oxygen partial pressure can be reduced using a sweep gas. In this case we consider nitrogen, which can be produced via cryogenic rectification. This gives nitrogen gas with an oxygen impurity concentration of 1 ppm, with an electrical energy cost of approximately 15 kJ mol^{-1} [45]. Assuming that heat can be converted to electricity with an efficiency of 40 %, the cost of producing nitrogen for the reduction of one mole of ceria is

$$Q_{N_2} = n_{N_2} \times 37500 \quad [J\,mol^{-1}], \tag{11}$$

where n_{N_2} is the number of moles of nitrogen used per mole of ceria cycled and 37500 J mol^{-1} = $\frac{15\,\mathrm{kJ\,mol^{-1}}}{0.4}$.

The minimum n_{N_2} can be calculated by assuming that all of the oxygen released during reduction is at equilibrium conditions and that the sweep gas is only used when the reactor reaches T_{rd}. This gives the minimum since if the partial pressure is increased past equilibrium the reaction can no longer proceed, and the equilibrium partial pressure is largest at the upper temperature T_{rd}.

An important aspect of using a sweep gas is that it must be heated to the reduction temperature. The gas leaving the reactor can be used to heat the sweep gas entering the reactor via a heat exchanger. The energy cost of heating the sweep gas is then

$$Q_{gas} = (1 - \varepsilon_{gas})\left(n_{N_2} \int_{T_{amb}}^{T_{rd}} C_{p_{N_2}}(T)dT\right) \quad [Jmol^{-1}], \tag{12}$$

where ε_{gas} is the heat exchanger effectiveness. The specific heat capacity of nitrogen as a function of temperature was obtained from the work of McBride *et al.* [46] and fit with a polynomial, which is given in the supporting material.

2.3. Pumping

If the system is maintained at lower than atmospheric pressure there is additional energy needed to pump the gases. It makes sense to only pump once the reactor has reached T_{rd}, as this maximises the oxygen partial pressure $P_{O_2}(\delta, T)$, and thus reduces the amount of pumping work necessary.

Here we consider the optimal case, where the oxygen is pumped at its equilibrium pressure if this is greater than the target operating pressure. The upper pressure is restricted to a maximum of ambient pressure giving a pumping pressure of

$$P_{pmp}(\delta, T) = \begin{cases} P_{amb} & : P_{O_2}(\delta, T) > P_{amb} \\ P_{O_2}(\delta, T) & : P_{amb} > P_{O_2}(\delta, T) > P \\ P & : P_{O_2}(\delta, T) \leq P \end{cases} \tag{13}$$

The energy required to pump is assumed to be that of pumping an ideal gas

$$\frac{\partial Q_{pmp}}{\partial \delta} = \frac{1}{2}\frac{RT}{\eta_{pmp}(P_{pmp})} \ln\left(\frac{P_{pmp}(\delta, T_{rd})}{P_{amb}}\right), \tag{14}$$

where the factor of one half accounts for half a mole of oxygen gas for one mole of vacancies. The total energy required to pump the gases is

$$Q_{pmp} = \int_{\delta_{ox}(\alpha)}^{\delta_{rd}} \frac{\partial Q_{pmp}}{\partial \delta} d\delta + \frac{n_{gas}(1 - \bar{x}_{O_2})RT}{\eta_{pmp}(P)} \ln\left(\frac{P}{P_{amb}}\right), \tag{15}$$

where the first term is that of pumping the oxygen, and the second term is the energy required to pump the sweep gas which is only used when the pressure reaches the lower value of P. The gas is assumed to be at a temperature of 70 °C during pumping. Note that the pumping efficiency η_{pmp}, is given a pressure dependence which is explained later.

2.4. Oxidation

Finally, we have the energy costs of oxidation, which is the cost of heating the oxidiser H_2O. The oxidation is assumed to take place at ambient pressure. Calculations for the minimum quantity of H_2O required to oxidise ceria from δ_{rd} to $\delta_{ox}(\alpha)$ are given in the supporting material. This calculation consists of first determining the ratio between H_2 and H_2O for steam in equilibrium with $CeO_{2-\delta}$. This gives the amount of oxidiser required for an infinitesimal change in δ, from which the total amount of oxidiser is calculated by integrating from δ_{rd} to $\delta_{ox}(\alpha)$.

A heat exchanger can be used to heat the oxidiser using the out flowing oxidiser and fuel. The energy required for oxidation is then given by

$$Q_{H_2O} = n_{H_2O}(1 - \epsilon_{gas})\left(\int_{100}^{T_{ox}} C_{p_{H_2O}}(T)dT + L_{H_2O}\right), \tag{16}$$

where L_{H_2O} is the latent heat of vaporisation of water. The same heat exchanger efficiency as that of the sweep gas heat exchanger is used for simplicity. This is a modest assumption as some of the heat released during oxidation ($Q_{rd} - \alpha\Delta\delta_{eq}\mathrm{HHV}_{H_2}$), should also be available for heating the oxidiser. This is accounted for later in the heat recovery section.

2.5. Plant efficiency

In order to account for losses consider that, for a given fuel production plant, the heat required to power all of the processes can be collected and supplied with an efficiency η_{plant}. This is to account for losses in solar collection and thermal losses due to re-radiation. It can be defined as

$$\eta_{plant}(T_{rd}, C) = \frac{0.9(1\,\mathrm{kW} \times C - \sigma(T_{rd}^4 - T_{amb}^4))}{1\,\mathrm{kW} \times C}, \tag{17}$$

where C is the solar concentration and the factor of 0.9 is to account for 10 % losses from the solar collectors. Note that this assumes that all the process heat is supplied to the reactor at temperature T_{rd}. This is a modest assumption as temperature swing cycles can be at lower temperatures during the heating phase, and some of the processes (Q_{pmp}, Q_{H_2O} and Q_{N_2}) could be supplied with heat at lower temperatures.

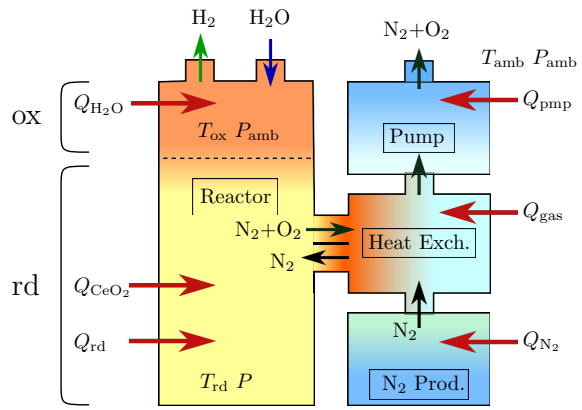

Figure 5: A schematic of the reactor showing the processes involved in reduction, their heat costs, and the flow of the nitrogen gas and the cycle products. Details of the processes are given in the text.

Figure 5 shows the various processes and heat inputs required for fuel production. With all of the energy costs, the fuel production efficiency can can now be defined as

$$\eta_{\text{fuel}} = \frac{\eta_{\text{plant}}\alpha\Delta\delta_{\text{eq}}\text{HHV}_{\text{H}_2}}{Q_{\text{rd}} + Q_{\text{CeO}_2} + Q_{\text{N}_2} + Q_{\text{gas}} + Q_{\text{pmp}} + Q_{\text{H}_2\text{O}}}. \quad (18)$$

If the system is at ambient pressure then $Q_{\text{pmp}} = 0$ and if the system is pumped to the target lower oxygen partial pressure ($P = P_{fO_2}$) then no sweep gas is needed and $Q_{\text{N}_2} = Q_{\text{gas}} = 0$.

η_{pmp}	0.15
ε_{gas}	0.75
C	3000

Table 1: Initial values for efficiency and solar concentration.

The values for the process efficiencies and solar concentration were fixed and are displayed in table 1. It seems feasible that the heat exchanger could have an effectiveness of 0.75, providing 75% of the heat needed for the sweep gas and oxidiser. Initially an efficiency of 15% is used for η_{pmp} with a more in-depth analysis of pumping and the pumping efficiency given in the next section.

3. Results

If the system is operated at ambient pressure there should be a value of P_{fO_2} which maximises the efficiency due to the trade off between the sweep gas processing ($Q_{\text{N}_2} + Q_{\text{gas}}$) costs and the amount of fuel produced ($\alpha\Delta\delta_{\text{eq}}$). For isothermal cycles the sheer quantities of sweep gas and oxidiser required (see supporting information) means the efficiency will be very low, and so we initially focus on temperature swing cycles.

3.1. Ambient pressure reduction

For the initial results of reduction at atmospheric pressure the value $\Delta T = 500$ °C was used, as this was close to the optimal value. For all results the fraction complete for the oxidation reaction was set to $\alpha = 0.95$, as this was approximately the optimal value and stopping the reaction any sooner only reduced the yield without increasing the efficiency. The calculated values of the fuel production efficiency for a range of values of T_{rd} are shown in figure 6. Each curve has a peak efficiency, and the position of the peak depends on T_{rd}. The peak is due to a trade off between the amount of energy stored in the fuel ($\alpha\Delta\delta_{\text{eq}}\text{HHV}_{\text{H}_2}$) and the energy needed to reduce the partial pressure ($Q_{\text{gas}} + Q_{\text{N}_2}$). Decreasing P_{fO_2} increases the energy stored in the fuel but also increases the energy needed for the sweep gas, which eventually increases much faster becoming the dominant energy cost and causing the efficiency to approach zero.

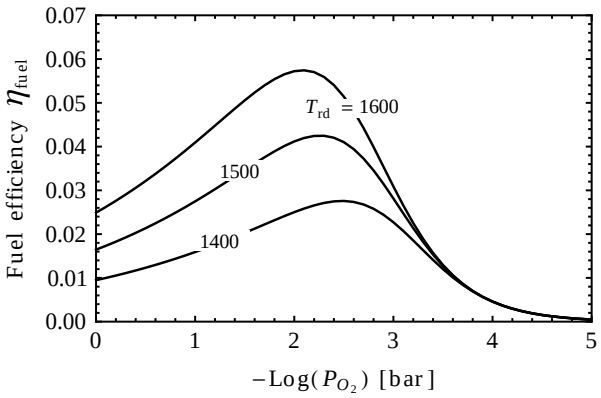

Figure 6: A plot of the η_{fuel} vs. $-log(P_{fO_2})$ for a range of values of T_{rd} (1400 1500 and 1600 °C), with $P = 1$ bar, $\Delta T = 500$ °C and $\alpha = 0.95$.

The optimal values of P_{fO_2} found here offer a very poor yield and low efficiency. Despite this, it is interesting to look at the effect of ΔT on the cycle efficiency when operated at ambient pressure. From figure 7 it can be seen that each cycle has an optimum ΔT. This is due to a balance between the amount of heat required for oxidation $Q_{\text{H}_2\text{O}}$, and the amount of heat that is needed to change the temperature of the ceria, Q_{CeO_2}. With increasing ΔT, $Q_{\text{H}_2\text{O}}$ decreases and up to a point $\alpha\Delta\delta_{\text{eq}}\text{HHV}_{\text{H}_2}$ increases. However, Q_{CeO_2} also increases and eventually increasing ΔT has a negative effect. For small enough ΔT the

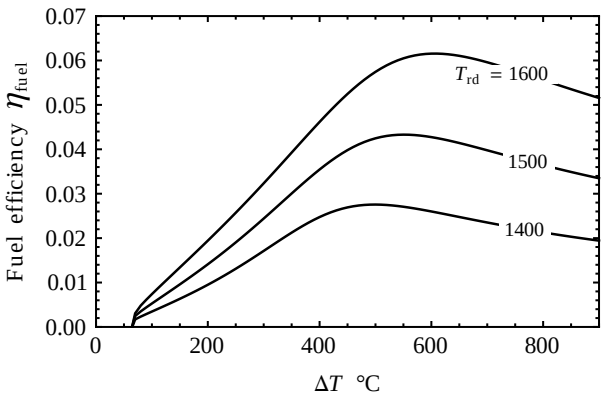

Figure 7: A plot of the η_{fuel} vs. ΔT for a range of values of T_{rd} (1400 1500 and 1600 °C), with $P = 1$ bar, $\Delta T = 500$ °C, $\alpha = 0.95$ and the peak values of P_{fO_2} from figure 6.

efficiency goes to zero due to the cycle yield becoming negative, i.e. $\alpha\Delta\delta_{eq} < 0$.

For a cycle with T_{rd} = 1500 °C, increasing ε_{gas} from 0.75 to 0.95 raised the maximum efficiency from approximately 4.5 to 5.5 % and shifted the optimal ΔT from around 500 to 400 °C. The increase is relatively small, as although Q_{gas} and Q_{H_2O} are greatly reduced, the energy required to produce the sweep gas is still very high. In any case, it is unlikely that gas phase heat exchangers with such high efficiencies could be developed for the temperatures considered.

3.2. Reducing the reduction operating pressure

Note that the value for η_{pmp} used here is given in table 1, as are the values of C and ε_{gas}. Figure 8 shows the effect of decreasing the operating pressure on the reactor efficiency. This was assumed to be the sole method of reducing the oxygen partial pressure, so that $Q_{N_2} = Q_{gas} = 0$. There is a maximum efficiency which is due to Q_{H_2O} decreasing with ΔT and Q_{CeO_2} increasing. This is very similar to the results obtained by Ermanoski *et al.* for temperature swing cycles [34].

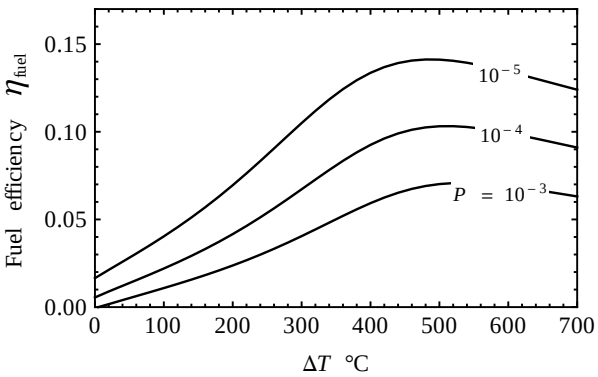

Figure 8: A plot of the η_{fuel} vs. the change in temperature ΔT for a range of values of reactor operating pressure P, with T_{rd} = 1500 °C, $P_{fO_2} = P$ and α = 0.95.

A pumping efficiency of 15% is very high for a pressure change of three to five orders of magnitude, so this result is not realistic. In reality the pumping efficiency will decrease with decreasing pressure. From the investigation of commercially available vacuum pumps (Busch vacuum pumps) an approximate value for the efficiency of the pump can be set. In figure 9 the pumping efficiency for some standard pumps is plotted on a log-log scale. The points form approximately a line which suggest that the efficiencies dependence on the pressure can be described with a power law.

At lower pressures the efficiency of the pumps is very low. However, the current vacuum pump industry is largely focused on simply maintaining low pressures without much interest in pumping efficiency. Efficiency improvements could likely be possible through the use of inter-cooling or the development of the more efficient axial flow type compressors for vacuum pumping. For this reason the pumping efficiency is assumed to be described by

$$\eta_{\text{elec to pump}}(P) = P^{0.544}, \tag{19}$$

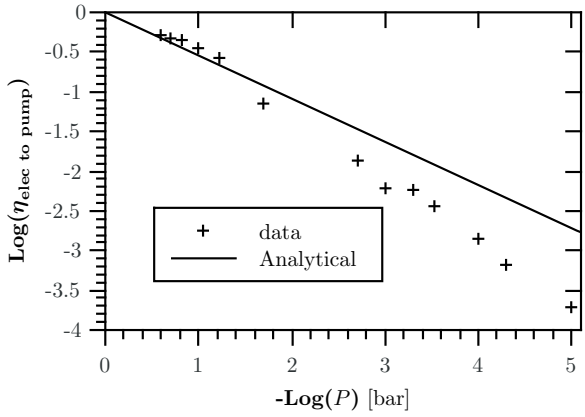

Figure 9: A plot of the $\log(\eta_{\text{pump to elec}})$ vs. -log(P) where the points are values calculated from commercially available pump specs, and the line is the analytical expression used in this work, with a slope of 0.544.

which is also plotted in figure 9. Assuming the conversion of heat to electricity has an efficiency of 40%, the pumping efficiency will then be

$$\eta_{pmp}(P) = 0.4\,\eta_{\text{elec to pump}}(P) = 0.4\,P^{0.544}. \tag{20}$$

If there is no pressure change the pumping efficiency approaches 40%, and at 10^{-5} bar the efficiency is almost an order of magnitude higher than the actual efficiency of the pumps investigated. The efficiency of an optimised axial flow compressor could be a lot higher, but the important fact here is that in general we would expect the pressure dependence of the efficiency to obey a power law.

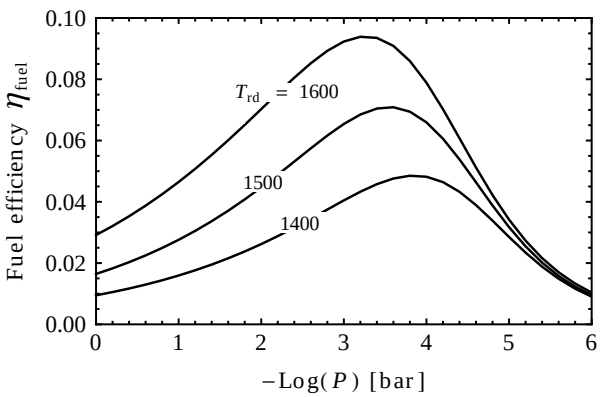

Figure 10: A plot of the η_{fuel} vs. -Log(P) for a range of values of T_{rd} (1400, 1500 and 1600 °C), with T_{ox} = 1000 °C, $P = P_{fO_2}$ and α = 0.95.

Figure 10 shows the effect of pumping the system to lower pressures with the new pumping efficiency. For each value of T_{rd} there is an optimal operating pressure P and reducing the pressure further decreases the efficiency. The peak efficiency here is substantially higher than for ambient pressure operation and it has a lower P_{fO_2} meaning a better yield. For the results shown here $P = P_{fO_2}$ and no sweep gas was used. It was found that using a sweep gas as well as pumping only reduced the

efficiency due to the high energy cost of producing the sweep gas.

Performing the reduction at lower than ambient pressure may have other benefits. Given that there is a net release of gas in the reduction reaction, there will be local pressure changes. These pressure changes can drive mass transport in the form of pressure wave propagation and pressure driven diffusion. Both of these processes should be more prominent at lower pressures as $\frac{\Delta P}{P}$ will increase. In addition if the ceria is formed into a porous monolith, which is often the case, the general diffusion gas phase mass transport also increases with decreasing pressure [47]. The reaction kinetics in a vacuum are very rapid, which can be seen in the previous work by the authors [39]. Many authors have measured much slower reaction kinetics at atmospheric pressure [48, 49, 50, 51, 52], which may be a result of restricted gas phase transport properties.

From this analysis we see that with some improvements to vacuum pumps, their use increases the efficiency as compared to using a sweep gas. The pump's pressure dependence means that there will be an optimal lower operating pressure to which the system should be pumped to during reduction. For the cycle conditions investigated here, optimal efficiency was around 7.5%.

3.3. Heat recovery

The heat used to change the temperature of the ceria (Q_{CeO_2}) has, up till now, been disregarded as lost heat. As discussed earlier there have been a number of designs suggested for exchanging this heat from the hot reduced ceria to the relatively cooler oxidised ceria [36, 37, 38]. These designs greatly increase reactor complexity and introduce some difficulties. They involve bringing the reduced and oxidised ceria into close proximity, which allows them to exchange oxygen. The oxidised and reduced ceria have different equilibrium oxygen partial pressures and when exposed to the same atmosphere they will exchange oxygen until they reach equilibrium. This will result in a decrease in both efficiency and yield.

A much more simple and sensible approach would be to try to convert the ceria heat Q_{CeO_2}, into process heat. This would involve cooling the ceria in a heat exchanger which should be much easier to achieve. The efficiencies calculated so far have been quite low due to the heat cost of the other processes (Q_{pmp} and Q_{H_2O} for a pumped reactor), and thus heat recovery in this way could offer significant improvements without the complication of ceria to ceria heat recuperation.

There is also a small quantity of heat released during oxidation

$$Q_{ox} = Q_{rd} - \alpha\Delta\delta_{eq}\mathrm{HHV}_{H_2} \tag{21}$$

, some of which could be recovered and used as process heat. The amount of recovered heat is limited by the total heat required for the lower temperature processes giving

$$Q_{rec} = \begin{cases} \varepsilon_{rec}(Q_{ox} + Q_{CeO_2}) & : Q_{pmp} + Q_{H_2O} > \varepsilon_{rec}(Q_{ox} + Q_{CeO_2}) \\ Q_{pmp} + Q_{H_2O} & : Q_{pmp} + Q_{H_2O} < \varepsilon_{rec}(Q_{ox} + Q_{CeO_2}) \end{cases}, \tag{22}$$

for a pumped reactor, where ε_{rec} is the effectiveness of the heat recovery and $Q_{ox} = Q_{rd} - \alpha\Delta\delta_{eq}HHV_{H_2}$. The fuel efficiency then becomes

$$\eta_{fuel} = \frac{\eta_{plant}\alpha\Delta\delta_{eq}\mathrm{HHV}_{H_2}}{Q_{rd} + Q_{CeO_2} + Q_{pmp} + Q_{H_2O} - Q_{rec}}, \tag{23}$$

where the recovered heat Q_{rec} is subtracted from the other heat costs.

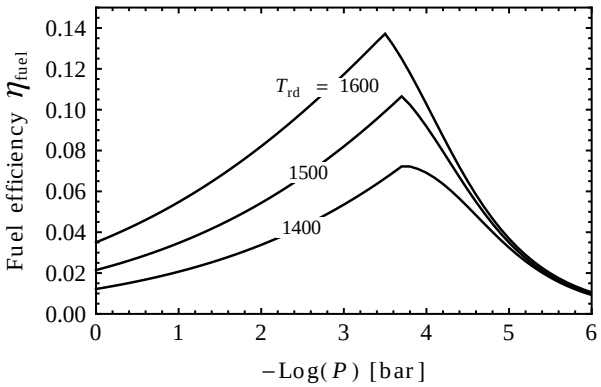

Figure 11: A plot of η_{fuel} vs. $-\log(P)$ for a range of values of T_{rd} (1400, 1500 and 1600 °C), with $\varepsilon_{rec} = 0.6$, $P = P_{fO_2}$, and $\alpha = 0.95$. The values of ΔT were 420, 520 and 580 °C respectively, which approximately optimised the efficiency.

Figure 11 shows the effect of recovering 60% of the heat from the hot ceria and from the oxidation reaction. The maximum efficiency occurs at a sharp kink, which is when the recovered heat is just enough to cover the lower temperature process heat ($Q_{pmp} + Q_{H_2O} = \varepsilon_{rec}(Q_{ox} + Q_{CeO_2})$). The efficiency was optimised with respect to ΔT and P giving a maximum of $\eta_{fuel} = 11\%$. The yield is also improved as the optimum pressure was lower when heat recovery was used.

4. Discussion

Calculations for CO_2 splitting gave very similar results to those seen for water splitting for temperature swing cycles. In general it required less CO_2 to oxidise the ceria and thus the efficiency was slightly higher. One drawback of CO_2 splitting is that a mixture of CO and CO_2 needs to be separated which was neglected in the calculations and would reduce the efficiency. Some select results for CO_2 splitting are presented in the supporting material.

4.1. Quantities of ceria

As mentioned earlier the total quantity of ceria which must be used in a reactor may be one of the major technical challenges preventing the implementation of the ceria cycle on a large scale. For a plant with an output power of $\dot{Q}_{out}$, the amount of ceria in moles per second which must be cycled is

$$\dot{n}_{CeO_2} = \frac{\dot{Q}_{out}}{\alpha\Delta\delta_{eq}\mathrm{HHV}_{H_2}} \quad [\mathrm{mol\,s^{-1}}], \tag{24}$$

and the total mass of ceria required per kilowatt output is given by

$$\frac{\partial m_{CeO_2}}{\partial \dot{Q}_{out}} = t_{cyc} M(CeO_2) \frac{\partial \dot{n}_{CeO_2}}{\partial \dot{Q}_{out}} \quad [\text{kg kW}^{-1}], \tag{25}$$

where t_{cyc} is the time it takes to complete one full cycle and $M(CeO_2)$ is the molar mass of ceria.

The time for one full cycle in the case of early prototypes was on the order of 50 min [16, 17]. For this reaction time, a cycle with T_{rd} = 1500 °C, operating at atmospheric pressure with the optimum efficiency conditions found above would require 138 kg of ceria per kW output with a peak efficiency of around 4.5%. Asides from the technical challenges associated with handling such quantities of ceria, the fuel output from a reactor using 138000 kg of ceria would not suffice to power a Toyota Prius engine (150 kW) [53], operating in parallel. This would make scaling up of this technology infeasible in terms of both cost and practicality. In order to reduce the quantity of ceria, the cycle time must be greatly reduced and the yield improved.

The majority of the cycle time in these early prototypes was spent on the reduction reaction. The kinetics of this reaction are very rapid [39], and thus this cycle time could be greatly improved upon. The yield can be improved by either increasing T_{rd} or decreasing P_{fO_2}. If more efficient pumps could be developed the optimal P_{fO_2} would decrease, increasing both the efficiency and yield.

As a very optimistic pumping scenario, one might assume that pumps similar to transonic or supersonic axial flow compressor with very high efficiency could be developed. These pumps which are under research for the aeronautics industry could offer compression ratios of 1.6 per stage with an efficiency of 85% per stage [54]. This would correspond to changing the pressure power factor in equation 20 from 0.54 to 0.27. For a cycle with T_{rd} = 1500 °C, ε_{rec} = 0.6, ε_{gas} = 0.75 and C = 3000, the maximised efficiency would then be approximately 16%. If the cycle time were 10 min this would give $\frac{\partial m_{CeO_2}}{\partial \dot{Q}_{out}}$ = 7 kg kW^{-1}, which is a great improvement, but still a rather large amount of ceria.

These findings may help to improve two step thermochemical fuel production cycles in general. For a given metal oxide cycle (MO_x), improving the efficiency and reducing $\frac{\partial m_{MO_x}}{\partial \dot{Q}_{out}}$ are likely the key issues which will decide the cycles success. If oxygen partial pressure must be reduced, then efficient vacuum pumps may be one of the main technology developments required to make the cycle competitive with other standard renewable fuel production methods, such as photovoltaic powered electrolysis.

These calculations neglect to take into account the use of dopants to improve the redox properties of ceria. The addition of both Zr and Hf to the ceria latice have been shown to increase the fuel production yield [55, 51]. These dopants also improve the high temperature stability of ceria allowing for a higher T_{rd}, meaning that such dopants could offer very significant improvements in η_{fuel} and n_{CeO_2}.

5. Conclusions

In this work the thermodynamics of CeO_2 thermochemical fuel production were analysed. For cycles operating at ambient pressure the maximum efficiency was found to be very low (≈ 4.5% for T_{rd} = 1500 °C) due to the very large amounts of sweep gas required to reduce the oxygen partial pressure. Isothermal cycles had very low efficiency under all conditions due to the excessive amounts of oxidiser required for the oxidation reaction.

The effect of performing the reduction at reduced pressures was investigated for pumps which have an efficiency that decreases with decreasing operating pressure. The results show the cycles have an optimal operating pressure and that using sweep gas as well as pumping only reduced the efficiency. Decreasing the pressure may offer other benefits. It improves the gas phase transport properties, which should improve the reduction kinetics. The optimal efficency, without solid state heat recovery, for a cycle operating at 1500 °C was found to be 7.5 %.

Instead of trying to recycle the heat from the ceria by exchanging it between hot and cold ceria, it is proposed this heat should simply be converted to process heat for powering the vacuum pumps and heating the oxidiser. With much more practical methods of heat recovery available, such as quenching the ceria in a heat exchanger this can offer significant efficiency gains.

Finally the amount of ceria which is needed per kW output power was investigated. For the normal cycle conditions considered, the amount of ceria required was extremely excessive and likely detrimental to any large scale implementation of this technology. Combined with the results of the efficiency, it seems that great improvements are needed if this cycle is to become competitive with more standard methods of renewable fuel production such as photovoltaic powered electrolysis. Some core technologies need to be developed, such as efficient vacuum pumps and high temperature heat exchangers for the oxidiser and for cooling the ceria. The use of dopants to improve both the yield and cycle time, would also improve both the efficiency and the practicality of the cycle.

Acknowledgements

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References

[1] Thomas F. Stocker and Dahe Qin. Climate change 2013, the physical science basis. Technical Report 5, Intergovernmental Panel on Climate Change, 2014.

[2] F. Christopher and O. Jean Pierre. Climate change 2014, impacts, adaptation, and vulnerability. Technical Report 5, Intergovernmental Panel on Climate Change, 2014.

[3] Tomas Hernandez-Tejeda and Roberta Quadrelli. Climate change 2014, mitigation of climate change. Technical Report 5, Intergovernmental Panel on Climate Change, 2014.

[4] S. Vazquez, S.M. Lukic, E. Galvan, L.G. Franquelo, and J.M. Carrasco. Energy storage systems for transport and grid applications. *Industrial Electronics, IEEE Transactions on*, 57(12):3881–3895, Dec 2010.

[5] Jan Kopyscinski, Tilman J. Schildhauer, and Serge M.A. Biollaz. Production of synthetic natural gas (sng) from coal and dry biomass a technology review from 1950 to 2009. *Fuel*, 89(8):1763 – 1783, 2010.

[6] John O'.M. Bockris. The hydrogen economy: Its history. *International Journal of Hydrogen Energy*, 38(6):2579 – 2588, 2013.

[7] T. Kodama. High-temperature solar chemistry for converting solar heat to chemical fuels. *Progress in Energy and Combustion Science*, 29(6):567 – 597, 2003.

[8] Aldo Steinfeld. Solar thermochemical production of Hydrogena review. *Solar Energy*, 78(5):603 – 615, 2005.

[9] Stphane Abanades, Patrice Charvin, Gilles Flamant, and Pierre Neveu. Screening of water-splitting thermochemical cycles potentially attractive for Hydrogen production by concentrated solar energy. *Energy*, 31(14):2805 – 2822, 2006.

[10] Martin Roeb, Martina Neises, Nathalie Monnerie, Friedemann Call, Heike Simon, Christian Sattler, Martin Schmücker, and Robert Pitz-Paal. Materials-related aspects of thermochemical water and carbon dioxide splitting: A review. *Materials*, 5(11):2015–2054, 2012.

[11] Tatsuya Kodama and Nobuyuki Gokon. Thermochemical cycles for high-temperature solar Hydrogen production. *Chemical Reviews*, 107(10):4048–4077, 2007.

[12] R.J. Panlener, R.N. Blumenthal, and J.E. Garnier. A thermodynamic study of nonstoichiometric Cerium dioxide. *Journal of Physics and Chemistry of Solids*, 36(11):1213 – 1222, 1975.

[13] Stphane Abanades and Gilles Flamant. Thermochemical hydrogen production from a two-step solar-driven water-splitting cycle based on cerium oxides. *Solar Energy*, 80(12):1611 – 1623, 2006.

[14] Matvei Zinkevich, Dejan Djurovic, and Fritz Aldinger. Thermodynamic modelling of the Cerium Oxygen system. *Solid State Ionics*, 177(1112):989 – 1001, 2006.

[15] E.A. Kümmerle and G. Heger. The structures of CCe_2O_{3+}, Ce_7O_{12}, and $Ce_{11}O20$. *Journal of Solid State Chemistry*, 147(2):485–500, 1999.

[16] William C. Chueh, Christoph Falter, Mandy Abbott, Danien Scipio, Philipp Furler, Sossina M. Haile, and Aldo Steinfeld. High-flux solar-driven thermochemical dissociation of CO_2 and H_2O using nonstoichiometric Ceria. *Science*, 330(6012):1797–1801, 2010.

[17] Philipp Furler, Jonathan R. Scheffe, and Aldo Steinfeld. Syngas production by simultaneous splitting of H_2O and CO_2 via ceria redox reactions in a high-temperature solar reactor. *Energy Environ. Sci.*, 5:6098–6103, 2012.

[18] Stephen G. Rudisill, Luke J. Venstrom, Nicholas D. Petkovich, Tingting Quan, Nicholas Hein, Daniel B. Boman, Jane H. Davidson, and Andreas Stein. Enhanced oxidation kinetics in thermochemical cycling of CeO_2 through templated porosity. *The Journal of Physical Chemistry C*, 117(4):1692–1700, 2013.

[19] Mark E. Dry. High quality diesel via the FischerTropsch process a review. *Journal of Chemical Technology & Biotechnology*, 77(1):43–50, 2002.

[20] Mark E Dry. The fischertropsch process: 19502000. *Catalysis Today*, 71(34):227 – 241, 2002.

[21] H.I. Villafán-Vidales, C.A. Arancibia-Bulnes, U. Dehesa-Carrasco, and H. Romero-Paredes. Monte Carlo radiative transfer simulation of a cavity solar reactor for the reduction of Cerium oxide. *International Journal of Hydrogen Energy*, 34(1):115 – 124, 2009.

[22] B. Bulfin, B.E. Murphy, O. Lubben, S.A. Krasnikov, and I.V. Shvets. Finite element method simulations of heat flow in fixed bed solar water splitting redox reactors. *International Journal of Hydrogen Energy*, 37(13):10028 – 10035, 2012.

[23] Ivan Ermanoski, Nathan P. Siegel, and Ellen B. Stechel. A new reactor concept for efficient solar-thermochemical fuel production. *Journal of Solar Energy Engineering*, 135(3):031002 – 031010, 2013.

[24] Anis Houaijia, Christian Sattler, Martin Roeb, Matthias Lange, Stefan Breuer, and Jan Peter Säck. Analysis and improvement of a high-efficiency solar cavity reactor design for a two-step thermochemical cycle for solar hydrogen production from water. *Solar Energy*, 97(0):26 – 38, 2013.

[25] Hiroshi Kaneko, Takao Miura, Akinori Fuse, Hideyuki Ishihara, Shunpei Taku, Hiroaki Fukuzumi, Yuuki Naganuma, and Yutaka Tamaura. Rotary-type solar reactor for solar Hydrogen production with two-step water splitting process. *Energy & Fuels*, 21(4):2287–2293, 2007.

[26] Nobuyuki Gokon, Tetsuro Mataga, Nobuyuki Kondo, and Tatsuya Kodama. Thermochemical two-step water splitting by internally circulating fluidized bed of $NiFe_2O_4$ particles: Successive reaction of thermal-reduction and water-decomposition steps. *International Journal of Hydrogen Energy*, 36(8):4757 – 4767, 2011.

[27] J. Lapp, J.H. Davidson, and W. Lipiński. Efficiency of two-step solar thermochemical non-stoichiometric redox cycles withheat recovery. *Energy*, 37(1):591 – 600, 2012.

[28] Nathan P Siegel, James E Miller, Ivan Ermanoski, Richard B Diver, and Ellen B Stechel. Factors affecting the efficiency of solar driven metal oxide thermochemical cycles. *Industrial & Engineering Chemistry Research*, 52(9):3276–3286, 2013.

[29] Martin Roeb and Christian Sattler. Isothermal water splitting. *Science*, 341(6145):470–471, 2013.

[30] Roman Bader, Luke J. Venstrom, Jane H. Davidson, and Wojciech Lipiński. Thermodynamic analysis of isothermal redox cycling of ceria for solar fuel production. *Energy & Fuels*, 27(9):5533–5544, 2013.

[31] Jonathan R. Scheffe, Michael Welte, and Aldo Steinfeld. Thermal reduction of ceria within an aerosol reactor for h2o and co2 splitting. *Industrial & Engineering Chemistry Research*, 53(6):2175–2182, 2014.

[32] Christopher L. Muhich, Brian W. Evanko, Kayla C. Weston, Paul Lichty, Xinhua Liang, Janna Martinek, Charles B. Musgrave, and Alan W. Weimer. Efficient generation of H_2 by splitting water with an isothermal redox cycle. *Science*, 341(6145):540–542, 2013.

[33] Luke J Venstrom, Robert M De Smith, Yong Hao, Sossina M Haile, and Jane H Davidson. Efficient splitting of co2 in an isothermal redox cycle based on ceria. *Energy & Fuels*, 28(4):2732–2742, 2014.

[34] I. Ermanoski, J. E. Miller, and M. D. Allendorf. Efficiency maximization in solar-thermochemical fuel production: challenging the concept of isothermal water splitting. *Phys. Chem. Chem. Phys.*, 16:8418–8427, 2014.

[35] Ivan Ermanoski. Cascading pressure thermal reduction for efficient solar fuel production. *International Journal of Hydrogen Energy*, 39(25):13114–13117, 2014.

[36] James E. Miller, Mark D. Allendorf, Richard B. Diver, Lindsey Evans, Nathan P. Siegel, and John Stuecker. Metal oxide composites and structures for ultra-high temperature solar thermochemical cycles. *Journal of Materials Science*, 43:4714–4728, 2008.

[37] Richard B. Diver, James E. Miller, Mark D. Allendorf, Nathan P. Siegel, and Roy E. Hogan. Solar thermochemical water-splitting ferrite-cycle heat engines. *Journal of Solar Energy Engineering*, 130(4):041001–041009, 2008.

[38] Justin Lapp, Jane H Davidson, and Wojciech Lipiński. Heat transfer analysis of a solid-solid heat recuperation system for solar-driven nonstoichiometric redox cycles. *Journal of Solar Energy Engineering*, 135(3):031004, 2013.

[39] B. Bulfin, A. J. Lowe, K. A. Keogh, B. E. Murphy, O. Lubben, S. A. Krasnikov, and I. V. Shvets. Analytical model of ceo2 oxidation and reduction. *The Journal of Physical Chemistry C*, 117(46):24129–24137, 2013.

[40] P. Campserveux, J; Gerdanian. Thermodynamic study of the oxide CeO_{2-x} for 1. 5 < O/Ce < 2. *J. Solid state Chem.*, (73-92), 1978.

[41] Tadashi Sugihara Kenzo Kitayama, Kiyoshi Nojiri and Takashi Katsura. Phase equilibria in the CeO and CeFeO systems. *Journal of Solid State Chemistry*, 56(1):1 – 11, 1985.

[42] Bunji Iwaski and Takashi Katsura. The thermodynamic properties of the nonstoichiometric ceric oxide at temperatures from 900 to 1,300 °C. *Bulletin of the Chemical Society of Japan*, 44:1297–1301, 1970.

[43] J. William Dawicke and Robert N. Blumenthal. Oxygen association pressure measurements on nonstoichiometric Cerium dioxide. *Journal of The Electrochemical Society*, 133(5):904–909, January 1986.

[44] L. B. Pankratz and R. V. Mrazek. Thermodynamic properties of elements and oxides. *US Bureau of Mines Bulletin*, 672, 1982.

[45] Aldo Belloni, Christine Ahner, and Heinz-Wolfgang Häring. *Industrial Gases Processing*. John Wiley & Sons, 2008.

[46] Bonnie J. McBride, Sanford Gordon, and Martin A. Reno. Thermodynamic data for fifty reference elements. *NASA Technical Paper*, 3287, 1993.

[47] Donald G Aronson. The porous medium equation. In *Nonlinear diffusion problems*, pages 1–46. Springer, 1986.

[48] Alex Le Gal and Stphane Abanades. Catalytic investigation of Ceria-Zirconia solid solutions for solar Hydrogen production. *International Journal of Hydrogen Energy*, 36(8):4739 – 4748, 2011.

[49] Alex Le Gal, Stphane Abanades, and Gilles Flamant. CO_2 and H_2O splitting for thermochemical production of solar fuels using nonstoichiometric Ceria and Ceria/Zirconia solid solutions. *Energy & Fuels*, 25(10):4836–4845, 2011.

[50] Alex Le Gal and Stphane Abanades. Dopant incorporation in ceria for enhanced water-splitting activity during solar thermochemical hydrogen generation. *The Journal of Physical Chemistry C*, 116(25):13516–13523, 2012.

[51] Qing-Long Meng, Chong il Lee, Toshihiko Ishihara, Hiroshi Kaneko, and Yutaka Tamaura. Reactivity of CeO_2-based ceramics for solar Hydrogen production via a two-step water-splitting cycle with concentrated solar energy. *International Journal of Hydrogen Energy*, 36(21):13435 – 13441, 2011.

[52] Qing-Long Meng, Chong il Lee, Satoshi Shigeta, Hiroshi Kaneko, and Yutaka Tamaura. Solar hydrogen production using $Ce_{1x}Li_xO_2$ solid solutions via a thermochemical, two-step water-splitting cycle. *Journal of Solid State Chemistry*, 194(0):343 – 351, 2012.

[53] Koichiro Muta, Makoto Yamazaki, and Junji Tokieda. Development of new-generation hybrid system ths ii-drastic improvement of power performance and fuel economy. Technical report, SAE Technical Paper, 2004.

[54] Boyce Meherwan. P.(2006), 2.0 axial-flow compressors. *The Gas Turbine Handbook*.

[55] Friedemann Call, Martin Roeb, Martin Schmücker, Hlne Bru, Daniel Curulla-Ferre, Christian Sattler, and Robert Pitz-Paal. Thermogravimetric analysis of zirconia-doped ceria for thermochemical production of solar fuel. *American Journal of Analytical Chemistry*, 4(10A):37–45, 2013.