

Thermodynamics of CeO₂ thermochemical fuel production - Supporting Information

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Abstract

In this supporting document the equilibrium oxygen partial pressure as a function of temperature in 1 bar of both H₂O and CO₂ is calculated. In addition the minimum quantities of both sweep gas and oxidiser for a given cycle are calculated using equilibrium considerations. Some select results for CO₂ splitting are also given.

Nomenclature

δ Oxygen stoichiometry

ΔH Change in enthalpy

ΔS Change in entropy

ΔG Change in Gibbs free energy

K_a Equilibrium constant

T_{rd} Reduction temperature

T_{ox} Oxidation temperature

ΔT $T_{rd} - T_{ox}$

δ_{rd} Reduced stoichiometry

δ_{ox} Oxidized stoichiometry

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$\Delta\delta_{\text{eq}}$ Equilibrium yield

P_{O_2} Oxygen partial pressure

$P_{f\text{O}_2}$ Final P_{O_2} during reduction

C_p Specific heat capacity

x_i Mole fraction of species i

n_i Moles of species i

α Fraction completed for oxidation reaction

a_i Activity of species i

$R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}$ Equilibrium ratio between H_2 and H_2O in contact with $\text{CeO}_{2-\delta}$

1. Oxygen partial pressure in steam

Specific heat capacities are given in table 2 and standard Gibbs energy and enthalpy of formation are given in table 1.

$\text{H}_2\text{O} \longrightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$	$\Delta H_f^\circ = 241.82 \text{ [kJmol}^{-1}\text{]}$	$\Delta G_f^\circ = 228.61 \text{ [kJmol}^{-1}\text{]}$
$\text{CO}_2 \longrightarrow \text{CO} + \frac{1}{2}\text{O}_2$	$\Delta H_f^\circ = 283.00 \text{ [kJmol}^{-1}\text{]}$	$\Delta G_f^\circ = 257.23 \text{ [kJmol}^{-1}\text{]}$

Table 1: Standard change in enthalpy and Gibbs free energy at 298 K and 1 bar (SATP).

1.1. Oxygen partial pressure in oxidiser



The equilibrium constant for the water splitting reaction is

$$K_{\text{ws}}(T) = \frac{x_{\text{H}_2}x_{\text{O}_2}^{0.5}}{x_{\text{H}_2\text{O}}}, \quad (2)$$

where x represents the mole fractions of each species, and K_{ws} is the equilibrium constant. The value of the equilibrium constant at SATP can be calculated using the equation

$$K_{\text{ws}}^{\circ} = \exp\left(\frac{-\Delta G_f^{\circ}}{RT}\right), \quad (3)$$

and the standard change in Gibbs energy given in table 1.

The temperature dependence of the equilibrium constant is given by

$$\ln\left(\frac{K_{\text{ws}}(T)}{K_{\text{ws}}^{\circ}}\right) = \int_{298\text{ K}}^T \frac{\Delta H(T)}{RT^2} dT. \quad (4)$$

The temperature dependence of the change in enthalpy for water splitting can be determined from the energy required to raise the temperature of the steam compared to that of the products, which is

$$\Delta H(T) = \Delta H_f^{\circ} - \int_{298\text{ K}}^T C_{p\text{H}_2\text{O}}(T) - C_{p\text{H}_2}(T) - \frac{1}{2}C_{p\text{O}_2}(T) dT. \quad (5)$$

Polynomial fits of the specific heat capacities are given in table 2.

$C_{p\text{N}_2}(T)$	$28.12 + 8.059 \times 10^{-4} T + 6.882 \times 10^{-6} T^2 - 3.871 \times 10^{-9} T^3 + 6.104 \times 10^{-13} T^4$
$C_{p\text{O}_2}(T)$	$25.38 + 1.458 \times 10^{-2} T - 6.210 \times 10^{-6} T^2 + 1.012 \times 10^{-9} T^3$
$C_{p\text{H}_2}(T)$	$29.99 - 3.818 \times 10^{-3} T + 5.335 \times 10^{-6} T^2 - 1.161 \times 10^{-9} T^3$
$C_{p\text{C}_2\text{O}_2}(T)$	$37.10 + 0.113 T - 1.19 \times 10^{-4} T^2 + 5.69 \times 10^{-6} T^3 - 9.62 \times 10^{-10} T^4$
$C_{p\text{H}_2\text{O}}(T)$	$31.43 + 3.332 \times 10^{-3} T + 1.115 \times 10^{-5} T^2 - 5.448 \times 10^{-9} T^3 + 7.543 \times 10^{-13} T^4$
$C_{p\text{CO}_2}(T)$	$20.99 + 6.768 \times 10^{-2} T - 4.960 \times 10^{-5} T^2 + 1.779 \times 10^{-8} T^3 - 2.495 \times 10^{-12} T^4$
$C_{p\text{CO}}(T)$	$28.98 - 3.412 \times 10^{-3} T + 1.480 \times 10^{-5} T^2 - 8.959 \times 10^{-9} T^3 + 1.655 \times 10^{-12} T^4$

Table 2: Polynomial fits of specific heat capacities C_p [$\text{J mol}^{-1} \text{K}^{-1}$]. They were fit from 300 - 2300 K and the polynomial value was always within 1% of the literature value [1, 2]

Using equations 3, 4 and 5, $K_{\text{ws}}(T)$ can now be calculated for a given temperature. From the balanced reaction given in equation 1 the mole fractions of hydrogen and steam can be defined as $x_{\text{H}_2} = 2x_{\text{O}_2}$ and $x_{\text{H}_2\text{O}} = 1 - 3x_{\text{O}_2}$. These can be substituted into equation 2 to get

$$K_{\text{ws}}(T) = \frac{2x_{\text{O}_2}^{1.5}}{1 - 3x_{\text{O}_2}}. \quad (6)$$

Given that x_{O_2} at the temperatures considered ($T < 2000$ K) should be quite low, solving this condition iteratively once is enough to accurately determine x_{O_2} .

$$K_{\text{ws}}(T) = 2x'_{\text{O}_2}{}^{1.5} \quad x_{\text{O}_2}(T) = \left(K_{\text{ws}}(T) \frac{1 - 3x'_{\text{O}_2}}{2} \right)^{-1.5} \quad (7)$$

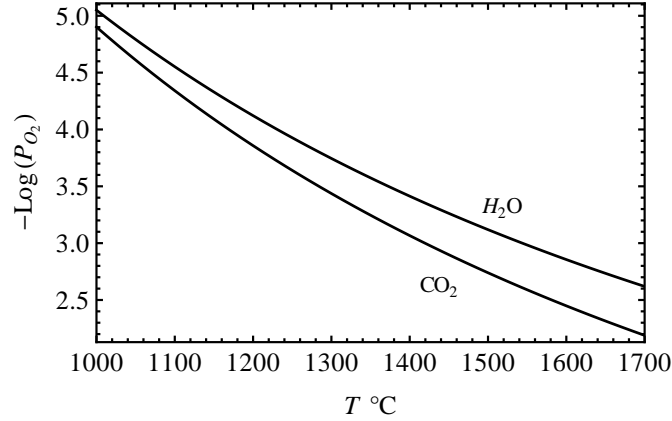


Figure 1: $-\text{Log}(P_{\text{O}_2})$ vs. temperature in 1 bar of steam and CO_2 .

The same procedure can be followed to compute the oxygen mole fraction in CO_2 as a function of temperature. The oxygen partial pressure is then simply the mole fraction multiplied by the total pressure.

1.2. Minimum quantity of sweep gas

As discussed in the manuscript the minimum quantity of sweep gas n_{N_2} can be calculated by assuming that all of the oxygen released during reduction is at equilibrium conditions. By rearranging the equation for the equilibrium vacancy concentration (equation 5 from the manuscript), the equilibrium P_{O_2} can be expressed as

$$P_{\text{O}_2}(\delta, T) = \left(\frac{8700(0.35 - \delta) \exp\left(\frac{-195.6 \text{ kJmol}^{-1}}{RT}\right)}{\delta} \right)^{\frac{1}{0.217}} \quad [\text{bar}], \quad (8)$$

and the mole fraction of released oxygen is then

$$x_{\text{O}_2}(\delta, T) = \frac{P_{\text{O}_2}(\delta, T) - 10^{-6}P}{P}, \quad (9)$$

where the $10^{-6}P$ is to account for the 1 ppm O_2 already in the sweep gas. The total number of moles of gas n_{gas} ($Q_{N_2} + Q_{O_2}$) per mole of vacancies created is then given by

$$\frac{\partial n_{\text{gas}}(\delta, T)}{\partial \delta} = \frac{1}{2x_{O_2}(\delta, T)}, \quad (10)$$

where $2x_{O_2}$ accounts for there being half a mole of O_2 per mole of vacancies. In addition, n_{gas} will be at a minimum if the sweep gas is only used to remove the oxygen when at the upper temperature T_{rd} , as the equilibrium P_{O_2} increases with temperature. The minimum n_{gas} , is then given by the normalised integral

$$n_{\text{gas}} = \frac{\int_{\delta_{\text{ox}}(\alpha)}^{\delta_{\text{rd}}} \frac{\partial n_{\text{gas}}(\delta, T)}{\partial \delta} d\delta}{\alpha \Delta \delta_{\text{eq}}}, \quad (11)$$

and thus the minimum number of moles of sweep gas is

$$n_{N_2} = n_{\text{gas}} - n_{O_2}, \quad (12)$$

where $n_{O_2} = \frac{\alpha \Delta \delta_{\text{eq}}}{2}$. The maximum average mole fraction of oxygen in the product stream is then

$$\bar{x}_{O_2} = \frac{\alpha \Delta \delta_{\text{eq}}}{2n_{\text{gas}}}. \quad (13)$$

It is necessary to introduce an additional condition on the value of P_{O_2} . If $P_{O_2} \geq P$, it must be set equal to the total pressure. In other words, in the case where no sweep gas is needed, the oxygen is just removed at the operating pressure of the reactor as it heats up, avoiding errors in the value of \bar{x}_{O_2} .

$$P_{O_2}(\delta, T) = \begin{cases} P_{O_2}(\delta, T) & : P_{O_2}(\delta, T) < P \\ P & : P_{O_2}(\delta, T) \geq P \end{cases} \quad (14)$$

The maximum average oxygen mole fraction is obtained in the same way except that in equation 9 the expression for P_{O_2} is given by equation 14. The value \bar{x}_{O_2} is very important as it determines the amount of sweep gas needed per mole of fuel produced, and hence can greatly effect the efficiency.

In figure 2, the results for the cycles with $\Delta T < 500$ stop abruptly as the cycle becomes impossible when $\Delta \delta_{\text{eq}} < 0$. For reduction operating at a total pressure of 1 bar, \bar{x}_{O_2} decreases with decreasing P_{fO_2} . The energy cost of producing nitrogen is quite high and thus cycles with low \bar{x}_{O_2} ($< 10^{-2}$) will

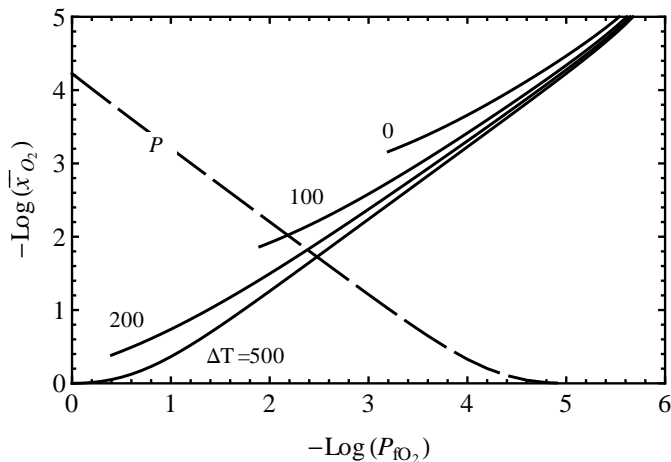


Figure 2: A plot of $-\log(\bar{x}_{O_2})$ vs. $-\log(P_{fO_2})$ with $T_{rd} = 1500$ °C. The solid lines are for a range of values of ΔT (0, 100, 200 and 500 °C) with $P = 1$ bar. The dashed line is a plot of $-\log(\bar{x}_{O_2})$ vs. $-\log(P)$, with $P_{fO_2} = 10^{-5}$ bar and $T_{rd} = 1500$ °C.

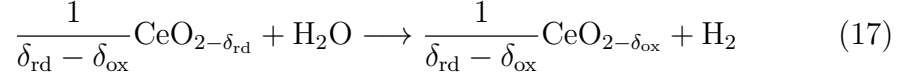
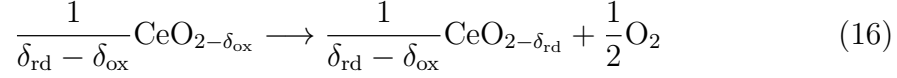
suffer from very poor efficiency. In order to obtain low P_{fO_2} it may be more sensible to pump the system to lower pressures, which reduces the amount of sweep gas needed. This is illustrated by the dashed line in figure 2.

It can be seen that with $P = 1$ bar isothermal cycles have minimum \bar{x}_{O_2} of $\approx 10^{-3}$, which will result in very poor efficiency. This appears to agree with the experimental demonstration of the isothermal cycle performed by Venstrom *et al.* [3], where ceria was reduced at 1500 °C using a sweep gas flow rate of $581 \text{ ml min}^{-1} \text{ g}^{-1}$ for 9.5 min resulting in a yield of $\Delta\delta = 0.01$ (see figure 5 in their manuscript), which corresponds to an \bar{x}_{O_2} of approximately 1.2×10^{-4} . Here the maximum \bar{x}_{O_2} was calculated to be 2.0×10^{-4} , for a cycle with $T_{rd} = 1500$ °C, $\alpha = 0.66$, $\Delta T = 0$, with a yield $\alpha\Delta\delta_{eq} = 0.01$ (these values were determined from the data presented in the Venstrom paper) and using CO_2 as the oxidiser. This maximum value is, as expected, greater than that obtained in practice by Venstrom *et al.* by a factor of 1.7. The maximum value is larger, but also comparable to the value obtained in practice offers good support for the calculation.

1.3. Minimum quantity of oxidiser

Here the amount of H_2O required to oxidise the ceria is calculated. First we must calculate the equilibrium mole fraction of H_2 for steam in equilibrium with $\text{CeO}_{2-\delta}$.

The reactions equations are given by the following.



The Gibbs free energies must add up to that of water splitting at any given temperature giving

$$\Delta G_{\text{ws}}(T) = \Delta G_{\text{rd}}(T) + \Delta G_{\text{ox}}(T). \quad (18)$$

Now using the equation $\Delta G = -RT \ln(K)$ and the equilibrium constants

$$K_{\text{rd}} = \frac{(a_{\text{O}_2})^{\frac{1}{2}}(a_{\text{CeO}_{2-\delta_{\text{rd}}})^{\frac{1}{\Delta\delta}}}{(a_{\text{CeO}_{2-\delta_{\text{ox}}})^{\frac{1}{\Delta\delta}}}} \quad K_{\text{ox}} = \frac{(a_{\text{H}_2})(a_{\text{CeO}_{2-\delta_{\text{ox}}})^{\frac{1}{\Delta\delta}}}{(a_{\text{H}_2})(a_{\text{CeO}_{2-\delta_{\text{rd}}})^{\frac{1}{\Delta\delta}}}}, \quad (19)$$

we can write equation 18 as

$$\Delta G_{\text{ws}}(T) = -RT \ln \left(\frac{(a_{\text{O}_2})^{\frac{1}{2}}(a_{\text{H}_2})(a_{\text{CeO}_{2-\delta_{\text{rd}}})^{\frac{1}{\Delta\delta}}(a_{\text{CeO}_{2-\delta_{\text{ox}}})^{\frac{1}{\Delta\delta}}}{(a_{\text{H}_2\text{O}})(a_{\text{CeO}_{2-\delta_{\text{ox}}})^{\frac{1}{\Delta\delta}}(a_{\text{CeO}_{2-\delta_{\text{rd}}})^{\frac{1}{\Delta\delta}}}} \right). \quad (20)$$

Simplifying and subbing in the partial pressures for the activities gives

$$\ln \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right) = \frac{-\Delta G_{\text{ws}}(T_{\text{ox}})}{RT} - \frac{1}{2} \ln(P_{\text{O}_2}(\delta, T_{\text{ox}})), \quad (21)$$

which can be re-arranged to give the equilibrium ratio between H_2 and H_2O as

$$R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}(\delta, T_{\text{ox}}) = \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \exp \left(\frac{-\Delta G_{\text{ws}}(T_{\text{ox}})}{RT_{\text{ox}}} - \frac{1}{2} \ln(P_{\text{O}_2}(\delta, T_{\text{ox}})) \right). \quad (22)$$

The value of $\Delta G_{\text{ws}}(T)$ can be calculated using $K_{\text{ws}}(T)$ from the previous section, and the formula $\Delta G = -RT \ln(K)$. Then using this value and the equilibrium oxygen partial pressure given in equation 8 $R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}$ can be calculated.

The equilibrium mole fraction of H₂ is

$$\frac{x_{\text{H}_2}}{1} = \frac{x_{\text{H}_2}}{x_{\text{H}_2\text{O}} + x_{\text{H}_2} + x_{\text{O}_2}} = \frac{\frac{x_{\text{H}_2}}{x_{\text{H}_2\text{O}}}}{\frac{x_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}}} + \frac{x_{\text{H}_2}}{x_{\text{H}_2\text{O}}} + \frac{x_{\text{O}_2}}{x_{\text{H}_2\text{O}}}} \approx \frac{R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}}{1 + R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}}, \quad (23)$$

since $x_{\text{H}_2\text{O}} + x_{\text{H}_2} + x_{\text{O}_2} = 1$ and $x_{\text{O}_2} \ll x_{\text{H}_2\text{O}} + x_{\text{H}_2}$. To get the mole fraction of hydrogen produced by the reaction with ceria, the equilibrium hydrogen in a pure steam atmosphere must also be subtracted giving

$$x_{\text{H}_2}(\delta, T_{\text{ox}}) = \frac{R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}(\delta, T_{\text{ox}})}{1 + R_{\frac{\text{H}_2}{\text{H}_2\text{O}}}(\delta, T_{\text{ox}})} - x_{\text{H}_2}(T_{\text{ox}})_{\text{eq}}, \quad (24)$$

where $x_{\text{H}_2}(T_{\text{ox}})_{\text{eq}}$ is the equilibrium mole fraction of hydrogen in an isolated H₂O atmosphere at temperature T_{ox} .

The minimum number of moles of oxidiser required per mole of fuel produced is then

$$\frac{\partial n_{\text{H}_2\text{O}}(\delta, T_{\text{ox}})}{\partial \delta} = \frac{1}{x_{\text{H}_2}(\delta, T_{\text{ox}})}, \quad (25)$$

with the total number of moles of oxidiser required to cycle one mole of ceria given by

$$n_{\text{H}_2\text{O}} = \frac{\int_{\delta_{\text{ox}}(\alpha)}^{\delta_{\text{rd}}} \frac{\partial n_{\text{H}_2\text{O}}(\delta, T_{\text{ox}})}{\partial \delta} d\delta}{\alpha \Delta \delta_{\text{eq}}}. \quad (26)$$

Figure 3 shows how \bar{x}_{H_2} depends on ΔT . For isothermal oxidation hundreds of moles of oxidiser are required to produce a mole of fuel, but this decreases rapidly for increasing ΔT . Decreasing the value of $P_{f\text{O}_2}$ also decreases the amount of oxidiser required, and where the lines abruptly stop is where operation becomes impossible as $\Delta \delta_{\text{eq}} < 0$. Stopping the oxidation at 95 % completion is also shown to greatly reduce the amount of oxidiser required.

The calculation was also performed for an oxidiser of CO₂, the results of which are given in figure 3. Again we can compare the results to the experimental demonstration of the isothermal cycle performed by Venstrom *et al.* [3], where ceria was oxidised in CO₂ at 1500 °C using an oxidiser flow rate of 297 ml min⁻¹g⁻¹ for 0.9 min, resulting in a yield of $\alpha \Delta \delta_{\text{eq}} = 0.01$, which corresponds to an \bar{x}_{CO} of approximately 5.3×10^{-3} . Here the maximum \bar{x}_{CO} was calculated to be 7.3×10^{-3} , for a cycle with $T_{\text{rd}} = 1500$ °C, $\alpha = 0.66$, $\Delta T = 0$, with a yield $\alpha \Delta \delta_{\text{eq}} = 0.01$. As before the value is larger

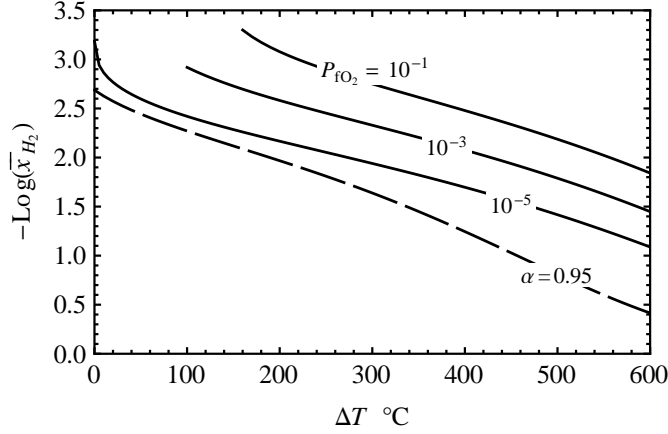


Figure 3: A plot of $-\log(\bar{x}_{H_2})$ vs. the change in temperature ΔT . The solid lines are different values of P_{fO_2} (10^{-1} , 10^{-3} and 10^{-5} bar) with $T_{rd} = 1500$ °C. The dashed line shows the effect of stopping the oxidation reaction before equilibrium at 95% completion, with $T_{rd} = 1500$ °C and $P_{fO_2} = 10^{-5}$ bar.

than that obtained in practice as expected, and the numbers are comparable which again offers support for the calculation. The low concentration of CO is very impractical as it must be separated from the product stream, which is not a trivial task. Together with sweep gas energy costs, these technical demands will make ambient pressure isothermal operation both impractical and very inefficient.

1.4. CO_2 splitting

The same calculation shown above can be made to determine $R_{\frac{CO}{CO_2}}$. There are a number of other differences to consider when calculating the efficiency of CO_2 splitting. The value of δ_{ox} needs to be changed throughout the calculations, as CeO_2 has a lower equilibrium vacancy concentration in CO_2 compared to water. In addition the heat required to sustain the oxidation reaction becomes

$$Q_{ox} = n_{CO_2}(1 - \epsilon_{gas}) \left(\int_{T_{amb}}^{T_{ox}} C_{pCO_2}(T) dT \right), \quad (27)$$

where $n_{CO_2} = \frac{1}{\bar{x}_{CO}}$.

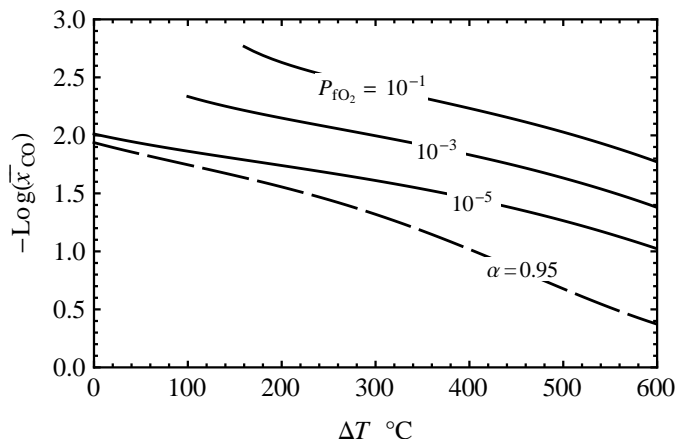


Figure 4: A plot of $-\log(\bar{x}_{\text{CO}})$ vs. the change in temperature ΔT . The solid lines are different values of $P_{f\text{O}_2}$ (10^{-1} , 10^{-3} and 10^{-5} bar) with $T_{\text{rd}} = 1500 \text{ } ^\circ\text{C}$. The dashed line shows the effect of stopping the oxidation reaction before equilibrium at 95 % completion, with $T_{\text{rd}} = 1500 \text{ } ^\circ\text{C}$ and $P_{f\text{O}_2} = 10^{-5}$ bar.

The calculation of \bar{x}_{CO} , was performed the same as that for \bar{x}_{H_2} , except using $R_{\frac{\text{CO}}{\text{CO}_2}}$ and δ_{ox} in CO_2 . This resulted in less oxidiser which can be seen by comparing figure 4 to figure 3. In general this gave slightly greater fuel production efficiency, which can be seen in figure 5. This is neglecting the fact that the product stream is a mixture of CO_2 and CO which needs to be separated.

References

- [1] Bonnie J. McBride, Sanford Gordon, and Martin A. Reno. Thermodynamic data for fifty reference elements. *NASA Technical Paper*, 3287, 1993.
- [2] L. B. Pankratz and R. V. Mrazek. Thermodynamic properties of elements and oxides. *US Bureau of Mines Bulletin*, 672, 1982.
- [3] Luke J Venstrom, Robert M De Smith, Yong Hao, Sossina M Haile, and Jane H Davidson. Efficient splitting of CO_2 in an isothermal redox cycle based on ceria. *Energy & Fuels*, 28(4):2732–2742, 2014.

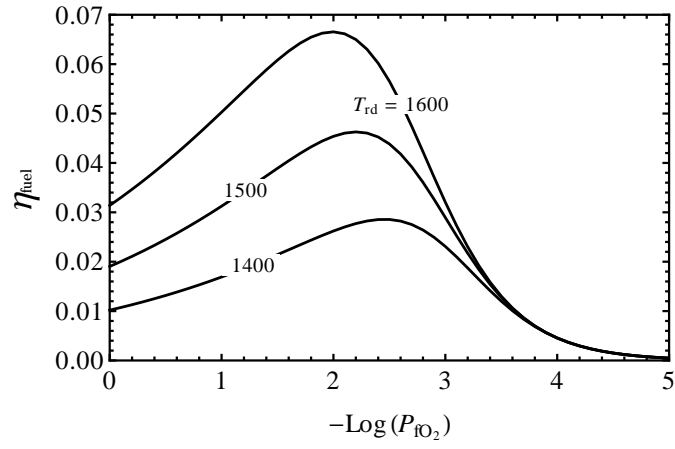


Figure 5: A plot of the η_{fuel} vs. $-\log(P_{f\text{O}_2})$ for a range of values of T_{rd} (1400 1500 and 1600 °C), with $P = 1$ bar, $\Delta T = 500$ °C, $\alpha = 0.95$ and using CO_2 as the oxidiser.