Combined Ceria Reduction and Methane Reforming in a Solar-Driven Particle-Transport Reactor

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ABSTRACT: We report on the experimental performance of a solar aerosol reactor for carrying out the combined thermochemical reduction of CeO2 and reforming of CH4 using concentrated radiation as the source of process heat. The 2 kWe88 solar reactor prototype utilizes a cavity receiver enclosing a vertical Al2O3 tube which contains a downward gravity-driven particle flow of ceria particles, either co-current or counter-current to a CH4 flow. Experimentation under a peak radiative flux of 2264 suns yielded methane conversions up to 89% at 1300 °C for residence times under 1 s. The maximum extent of ceria reduction, given by the nonstoichiometry δ(CeO2−δ), was 0.25. The solar-to-fuel energy conversion efficiency reached 12%. The syngas produced had a H2:CO molar ratio of 2, and its caloric value was solar-upgraded by 24% over that of the CH4 reformed.

1. INTRODUCTION

Thermochemical redox cycles driven by concentrated solar energy are a promising route to split H2O and CO2 and produce syngas,1-3 a mixture of H2 and CO that can be further processed to liquid hydrocarbon fuels via established gas-to-liquid processes. Nonstoichiometric ceria is currently considered the state of the art among nonvolatile redox materials because of its rapid kinetics and crystallographic stability.4-6 The two-step cycle comprises the endothermic reduction of ceria generally operated at above 1400 °C, followed by the lower-temperature exothermic reoxidation of ceria to its initial state with H2O and CO2 to form syngas. Various solar reactor concepts have been proposed for effecting this cycle, some of them experimentally demonstrated, including packed beds,7-8 porous structures,9-13 rotating components,14-16 and moving particles,17-20 that incorporated heat recovery during the temperature-swing mode or operated under isothermal mode. An intriguing approach to decrease the reduction temperature and thus the temperature swing between reduction and oxidation is to combine this redox cycle with the reforming of methane,21,22 according to the following:

Reduction-Reforming:

\[ \text{CeO}_2 + \delta \text{CH}_4 \rightarrow \text{CeO}_{2-\delta} + \delta (\text{CO} + 2\text{H}_2) \] (1)

Oxidation with \( \text{CO}_2/\text{H}_2\text{O} \):

\[ \text{CeO}_{2-\delta} + \delta \text{CO}_2 \rightarrow \text{CeO}_2 + \delta \text{CO} \] (2a)

\[ \text{CeO}_{2-\delta} + \delta \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \delta \text{H}_2 \] (2b)

During the endothermic reduction step (eq 1), CeO2 is reduced in the presence of CH4 to an extent given by the nonstoichiometry \( \delta \), where the required high-temperature heat is delivered by concentrated solar energy. The \( \delta \) moles of oxygen released from the ceria partially oxidize CH4 to form CO and H2.

In the subsequent exothermic oxidation step (eq 2), CeO2−δ reacts with CO2 or H2O to reincorporate oxygen into the lattice and form additional CO or H2, respectively. Reactions 2a and 2b intrinsically assume full oxidation at thermodynamically favorable temperatures below 1000 °C.23,24 Such a combined reduction-reforming processing using concentrated solar heat was previously proposed in the context of the co-production of metals and syngas.25,26 The introduction of a reducing agent such as CH4 during the reduction step effectively lowers the oxygen partial pressure and shifts the equilibrium to lower temperatures, below 1000 °C.21,22 Thus, it enables the operation of the two-step cycle isothermally, as demonstrated with a fixed bed reactor in the range 900-1000 °C.27 Using a similar fixed bed reactor in the range 400-800 °C, Pt was shown to catalyze the surface-controlled kinetics.28This concept is similar to chemical looping combustion (CLC) or chemical looping reforming (CLR) processes that also utilize metal oxides as an intermediate.29-31 The main advantage of these concepts compared to direct combustion or reforming is that the fuel and oxidant do not come into direct contact. Thus, in the case of CLC, CO2 can be generated without dilution in air, and in the case of CLR, high purity H2 or CO may be produced in the oxidation reactor without contamination by trace combustion gases. The main difference to the proposed concept is that, in CLC/CLR, the energy for endothermic reduction of the metal oxide is typically supplied by fuel combustion while the proposed concept aims at utilizing concentrated solar energy as the source of high-temperature process heat. The advantage to using ceria as a redox intermediate...
compared to other oxides is related to its rapid kinetics, favorable thermodynamics, and selectivity, as discussed in depth by Krenzcke et al.\textsuperscript{27} and Warren et al.\textsuperscript{22}

Dry reforming and steam reforming of methane driven by solar energy have also been investigated intensively,\textsuperscript{35} most recently by Weng et al.\textsuperscript{36} In contrast, the proposed combined reduction-reforming process does not require the use of catalysts, even for dry reforming. For example, the oxidation of ceria in the presence of CO\textsubscript{2} is known to be totally selective to CO\textsubscript{2} production.\textsuperscript{3,9,11} As such, a wide range of synthesis gas ratios (CO:H\textsubscript{2} between 1:1 and 1:3) are achievable without the need for a downstream water–gas shifting reactor by co-feeding CO\textsubscript{2} and H\textsubscript{2}O during the oxidation step.\textsuperscript{13}

We recently proposed a solar particle-transport reactor concept based on a cavity-receiver enclosing an array of aluminia tubes, each containing a downward flow of ceria particles counter to an inert sweep gas flow.\textsuperscript{17,18} This concept offers in situ separation of the solid and gas products, enhanced heat and mass transfer, good scalability due to the modular tubular configuration, and continuous operation of the reduction step. It further offers the possibility to individually design the (nonsolar) oxidation reactor and operate it independently and round-the-clock in combination with a particle storage. Possible configurations for an oxidation reactor include but are not limited to riser reactors and moving bed reactors. However, because of the indirect heat transfer to the reaction site by conduction through the Al\textsubscript{2}O\textsubscript{3} tube and convection–radiation to the particle flow, tube temperatures of 1500 °C and above were required for the effective reduction of ceria particles in short residence times. This critical temperature requirement can be significantly alleviated by the combined reduction-reforming approach.

In this work, we report on the experimental performance of the solar particle-transport reactor for the thermal reduction of ceria particles with CH\textsubscript{4}. We study the impact of temperature, ceria particle mass flow rate, gas flow rate, and CH\textsubscript{4} concentration on the extent of ceria reduction, methane conversion, and syngas quality. An energy balance is carried out for each experimental run to determine the solar-to-fuel energy conversion efficiency. We further compare counter-current and co-current gas–particle flow configurations and investigate the reactor stability under steady-state operating conditions.

2. EXPERIMENTAL METHODS

The schematic of the lab-scale solar reactor is shown in Figure 1. It is composed of an Al\textsubscript{2}O\textsubscript{3} tube (Haldenwanger, ALSINT 99.7, D\textsubscript{out} = 52 mm, D\textsubscript{in} = 40 mm, L = 850 mm) vertically positioned inside a cavity receiver (100 mm × 100 mm × 250 mm). The cavity is lined with 76.2 mm-thick Al\textsubscript{2}O\textsubscript{3} insulation (Zircar Zirconia, Type BusterM-35) supported by a 5 mm-thick aluminum shell. High-flux radiation enters the cavity through a polished Al compound parabolic concentrator\textsuperscript{37} (CPC, half acceptance angle of 45°) positioned in front of the windowless 30 mm-diameter circular aperture.\textsuperscript{18} The incident radiative power is absorbed by internal multiple reflections, resulting in a cavity’s apparent absorptivity of 88%, determined by Monte Carlo ray tracing performed with the in-house code VEGAS.\textsuperscript{39}

Ceria particles (Chempur, 99.9% purity, D\textsubscript{50} = 40 μm) contained in a 2 kg reservoir were delivered to the alumina tube by means of a screw feeder with adjustable rotational speed and subsequently carried to the reaction zone by gravity. The feeder design limited the particle mass flow rate to 0.6 g s\textsuperscript{−1} to avoid reasonable dispersion and avoid severe fluctuations. A balance (Kern FKB 61L0.02, uncertainty < ±0.02 g) below the reaction zone at the exit of the tube enabled online measurements of the mass flow rate of reduced ceria particles m\textsubscript{CeO\textsubscript{2−δ}}. Electric mass flow controllers (Bronkhorst, F-201C, uncertainty < ±2%) were used to deliver Ar purge gas to the balance housing at the bottom and the feeder at the top. Additionally, two lateral gas connections above and below the reaction zone were implemented to obtain either a co-current or counter-current gas–particle flow through the reaction zone (material flows for both configurations indicated in Figure 1). The product gas composition was analyzed by infrared-based detectors (Siemens Ultramat 6, uncertainty < ±1%) for CO/CO\textsubscript{2}/CH\textsubscript{4}, a paramagnetic alternating pressure O\textsubscript{2} detector (Siemens Oxymat 6, uncertainty < ±1%) and a thermal conductivity-based H\textsubscript{2} detector (Siemens Calomat 6) and validated with gas chromatography (Varian 490, uncertainty < ±1%) measuring H\textsubscript{2}, O\textsubscript{2}, CO, CO\textsubscript{2}, and CH\textsubscript{4}. Undetectable species H\textsubscript{2}O and C were calculated through molar balances of the supplied CH\textsubscript{4} and measured product gases. The tube temperature distribution was measured on the outside by six shielded thermocouples type-B (uncertainty <0.25%); the average yielded the nominal tube temperature T\textsubscript{tube}. The temperature distribution of particles, the loading distribution of particles, and the velocity distribution of particles across the radius were not measured. These measurements are complex and require optical techniques to avoid interference with the flow, but optical access was not possible with this solar reactor configuration. Prior to each experimental run, the particles were exposed to air at 300 °C for more than 8 h to ensure a fully oxidized state (δ\textsubscript{i} = 0). Carbon contamination in the ceria particles was below 0.004 mol\textsubscript{C} mol\textsuperscript{−1} CeO\textsubscript{2}, as also verified by thermogravimetric analysis in air at 800 °C.

The experiments were carried out at the high-flux solar simulator (HFSS) of ETH Zurich. An array of seven Xe-arc lamps, coupled to truncated ellipsoidal reflectors, provided an external source of intense thermal radiation, mostly in the visible and infrared spectra, that closely approximated the heat transfer...
characteristics of highly concentrating solar systems such as towers and dishes. The radiative flux distribution at the aperture plane was measured with a calibrated CCD camera focused on a refrigerated Al2O3 plasma-coated Lambertian (diffusely reflecting) target. The total solar radiation input \( P_{\text{sol}} \) at the exit of the CPC was calculated by flux integration and verified by water calorimetry.

During a typical experimental run, the cavity receiver was heated by concentrated radiation to the desired \( T_{\text{tube}} \) in the range of 1150–1350 °C, while being purged with Ar to reduce the oxygen partial pressure below 200 ppmv. Once steady-state \( T_{\text{tube}} \) was reached, \( P_{\text{so}} \) was maintained within 1.1–1.6 kW for mean solar concentration ratios of 1556–2264 suns (1 sun = 1 kW m\(^{-2}\)). Ar purge flows of 0.5 and 1 L\(_{\text{N}}\) min\(^{-1}\) (SLPM) gas flow rates calculated at 273.15 K and 1 atm) were delivered to the feeder and the balance housing, respectively. An Ar/CH\(_4\) gas mixture was delivered to the lateral gas inlet at variable flow rates and concentrations to obtain the desired flow conditions in the reaction zone. Typical Re numbers of the gas flow were in the range 25–40, indicative of laminar regime. The CH\(_4\) concentration was limited to 10% because of lab safety regulations.

### 3. RESULTS AND DISCUSSION

**Representative Experiment.** Figure 2 shows the variation of the ceria mass flow rate (left axis) and CH\(_4\) inlet molar flow rate (right axis) alongside \( H_2, CO, CO_2, \) and CH\(_4\) outlet molar flow rates as a function of time during a representative experimental run. The subscript 0 indicates the inlet condition. Experimental conditions: \( T_{\text{tube}} = 1302 °C, \delta_{\text{final}} = 0.16, V_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1}, \) co-current flow configuration.

![Figure 2](image)

**Figure 2.** Ceria mass flow rate at average \( \dot{m}_{\text{CeO}_2} = 0.13 \text{ g s}^{-1} \) (\( \dot{n}_{\text{CeO}_2} = 44.2 \text{ mmol min}^{-1} \)) (left axis) and CH\(_4\) inlet/outlet, \( H_2, CO, \) and \( CO_2 \) molar flow rates (right axis) as a function of time during a representative experimental run. In this run, \( \dot{m}_{\text{CeO}_2} = 0.13 \text{ g s}^{-1} \) (\( \dot{n}_{\text{CeO}_2} = 44.2 \text{ mmol min}^{-1} \)) of ceria particles were fed for 9.5 min with a \( V_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1} \) flow of 10% CH\(_4\)–Ar (\( \dot{n}_{\text{CH}_4} = 9.0 \text{ mmol min}^{-1} \)) through the reaction zone at a constant \( T_{\text{tube}} \) of 1303 °C. After a short stabilization period, outlet flows of \( H_2, CO, CO_2, \) and unreacted CH\(_4\) reached steady-state even though \( \dot{m}_{\text{CeO}_2} \) fluctuated due to poor dispersion by the particle screw feeder. \( \dot{n}_{\text{CeO}_2} \) was calculated by \( \dot{m}_{\text{CeO}_2} = \dot{m}_{\text{CeO}_2,0} + M_o (\dot{n}_{\text{CO}} + 2\dot{n}_{\text{CO}_2} + \dot{n}_{\text{H}_2}) \), where \( \dot{m}_{\text{CeO}_2,0} \) is the mass flow rate of reduced ceria (online balance measurement), \( M_o \) denotes the molar mass of monatomic oxygen, and \( \dot{n}_i \) denotes the molar flow rate of species \( i \) (GC and feed gas flows measurements). During steady-state

\( \dot{n}_{\text{CH}_4} = 14 \text{ mmol min}^{-1}, \dot{n}_{\text{CO}} = 6 \text{ mmol min}^{-1}, \dot{n}_{\text{CO}_2} = 0.24 \text{ mmol min}^{-1}, \dot{n}_{\text{H}_2} = 0.75 \text{ mmol min}^{-1}, \dot{n}_{\text{C}} = 1.2 \text{ mmol min}^{-1}, \) and \( \dot{n}_{\text{CH}_4} = 1.4 \text{ mmol min}^{-1} \). The final nonstoichiometry, \( \delta_{\text{final}} = (\dot{n}_{\text{CO}} + 2\dot{n}_{\text{CO}_2} + \dot{n}_{\text{H}_2})/\dot{m}_{\text{CeO}_2} \), was 0.16. The methane conversion, \( \chi_{\text{CH}_4} = 1 - \dot{n}_{\text{CH}_4}/\dot{m}_{\text{CeO}_2} \), was 0.85.

**Effect of Ceria Mass Flow Rate.** The effect of \( \dot{m}_{\text{CeO}_2} \) on \( \delta_{\text{final}} \) at \( T_{\text{tube}} = 1302 °C, V_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1} \), and \( x_{\text{CH}_4} = 0.1 \) is shown in Figure 3a and b by filled squares for co-current and counter-current gas–particle flows, respectively. For both gas–particle flow configurations, \( \delta_{\text{final}} \) decreased with increasing \( \dot{m}_{\text{CeO}_2} \). Additionally, for the same \( \dot{m}_{\text{CeO}_2} \), counter-current flow resulted in a higher \( \delta_{\text{final}} \). For example, for \( \dot{m}_{\text{CeO}_2} = 0.13 \text{ g s}^{-1} \), \( \delta_{\text{final}} \) was 0.18 and 0.23 for co-current and counter-current gas–particle flow, respectively. For the investigated temperature range, a closed-system thermodynamic analysis indicates that, at equilibrium, \( \delta_{\text{eq}} \) approaches the stoichiometric ratio \( \delta_{\text{eq}} \approx \dot{n}_{\text{CH}_4}/\dot{m}_{\text{CeO}_2} \). \( \delta_{\text{eq}} \) is plotted in Figure 3a and b by the dashed red line. Interestingly, \( \delta_{\text{final}} > \delta_{\text{eq}} \) for \( \dot{m}_{\text{CeO}_2} > 0.2 \text{ g s}^{-1} \) with the co-current flow configuration and for all \( \dot{m}_{\text{CeO}_2} \) with the counter-current flow configuration. This apparent inconsistency is explained by comparing the measured product composition with the thermodynamic equilibrium composition. Figure 4a displays the equilibrium composition and corresponding ceria nonstoichiometry \( \delta_{\text{eq}} \) for the system CeO\(_2\) + 0.25CH\(_4\) as a function of temperature at 1 atm. Computations were carried out following the methodology outlined in Warren et al. and considered the following species: CeO\(_2\), CH\(_4\), H\(_2\), CO, CO\(_2\), C, and O\(_2\). For \( n_{\text{CH}_4} = 0.25 \text{ molCH}_4/\text{ molCeO}_2 \), \( \delta_{\text{eq}} \) increases with temperature until 1027 °C where it plateaus due to the complete CH\(_4\) conversion. Below this temperature, C formation derived from CH\(_4\) decomposition is thermodynamically favorable. Above this temperature, a shift from C to CO occurs as oxygen evolves from ceria. Syngas constitutes more than 99 mol % of the products at equilibrium with molar ratio H\(_2\)/CO approaching 2. H\(_2\)O and CO\(_2\) are minimal throughout the considered temperature span. Figure 4b evaluates the impact of syngas for initial molar fractions corresponding to the complete CH\(_4\) conversion (\( n_{\text{CH}_4} = 0.5 \text{ molCH}_4/\text{ molCeO}_2 \) and \( n_{\text{H}_2} = 0.25 \text{ molH}_2/\text{ molCeO}_2 \)). \( \delta_{\text{eq}} \) increases with temperature. However, in the absence of CH\(_4\), the gas composition contains increasing amounts of H\(_2\)O and CO\(_2\). Additionally, for a given temperature, \( \delta_{\text{eq}} \) is lower for reduction with syngas compared to that with CH\(_4\). Consequently, in the presence of CH\(_4\) (Figure 4a), no further reduction of ceria with products H\(_2\) and CO is possible in a closed system.

The measured product composition is plotted in Figure 5a and b for the co-current and counter-current flow configurations, respectively. For both configurations, \( x_{\text{H}_2} \) decreased and \( x_{\text{H}_2O} \) increased with increasing \( \dot{m}_{\text{CeO}_2} \) while all other molar fractions remained relatively constant. This shift from H\(_2\) to H\(_2\)O, which is more accentuated under the counter-current gas flow configuration, contradicts the thermodynamic prediction (Figure 4a). The formation of water is attributed to the reduction of ceria with H\(_2\), which is thermodynamically favorable in the absence of CH\(_4\) (Figure 4b). Thus, we hypothesize that ceria is reduced initially by H\(_2\) and then by CH\(_4\) to an extent larger than \( \delta_{\text{eq}} \). For the co-current flow configuration,
this is only possible if H₂ diffuses counter to the gas flow, which can be expected because of a low Peclet number of 0.77. For the counter-current flow configuration, unreduced ceria inherently comes in contact with produced syngas, resulting in a higher value of \( \delta_{\text{final}} \) at the same \( m_{\text{CeO}_2} \) as well as a stronger decrease in \( x_{\text{H}_2} \) with increasing \( m_{\text{CeO}_2} \). We recognize that \( \delta_{\text{final}} \) as defined previously is a superposition of the influence of different reducing species, namely, CH₄, H₂, and CO, and thus can be divided into their respective influence according to

\[
\delta_{\text{final}} = \frac{n_{\text{CO}} + n_{\text{CO}_2}}{n_{\text{CeO}_2}} + \frac{n_{\text{CO}}}{n_{\text{CeO}_2}} + \frac{n_{\text{H}_2\text{O}}}{n_{\text{CeO}_2}}
\]

\( \delta_{\text{CH}_4} \) isolates the nonstoichiometry resulting from the reduction with methane without considering the additional reducing agents H₂ and CO, and thus \( \delta_{\text{CH}_4} \leq \delta_{\text{eq}} \). \( \delta_{\text{CH}_4} \) is plotted in Figure 3a and b by the open red squares and closely follows the trend of \( \delta_{\text{eq}} \) for both flow configurations. Both configurations result in the same \( \delta_{\text{CH}_4} \) for a given mass flow rate and consequently equal \( X_{\text{CH}_4} \). This indicates that the reaction is not kinetically limited. The gain obtained in \( \delta_{\text{final}} \) by operating with counter-current flow configuration is a result of undesired reactions between ceria and product syngas. While the consumed syngas is regained during a subsequent oxidation step, these side reactions result in dilution of the product syngas with H₂O and CO₂, requiring energy intensive postprocessing. Consequently, the co-current gas particle flow configuration is considered to be superior and will be the focus of further investigation.

**Effect of Tube Temperature.** Figure 6a shows the impact of the nominal temperature of the Al₂O₃ tube on ceria nonstoichiometry (left axis) and corresponding methane conversion (right axis) for a ceria mass flow rate of \( m_{\text{CeO}_2} = 0.13 \text{ g s}^{-1} \), gas flow of \( V_{\text{CH}_4/\text{Ar}} = 2 \text{ L min}^{-1} \), inlet methane concentration of 10%, and co-current gas–particle flow. As \( T_{\text{tube}} \) was raised from 1150 to 1350 °C, \( \delta_{\text{final}} \) increased from 0.025 to 0.22, respectively, and \( X_{\text{CH}_4} \) increased from 0.39 to 0.89, respectively. With similar nonstoichiometries of 0.2 and 0.25, however, lower \( X_{\text{CH}_4} \) of 0.6 and 0.52 were obtained in packed bed reactors at ceria temperatures of 1000 and 1120 °C, respectively. This points to a significant difference between the measured tube wall temperature and the actual particle temperature. Similar to the results shown in Figure 3, \( \delta_{\text{final}} \) exceeds the predicted closed system equilibrium (dashed line), presumably due to the reaction of ceria particles with product gases H₂ and CO at \( T_{\text{tube}} = 1350 \text{ °C} \). All syngas consumed in this manner during the reduction step is reformed during the oxidation step and, consequently, results in no additional gain/loss in fuel yield. The uncertainty in \( \delta_{\text{final}} \) is estimated to be below 10% based on the standard deviation of measurements taken for 1250 and 1300 °C.
on consecutive days (Figure 6). It is mainly due to fluctuations in the ceria mass flow rate with time, as shown in Figure 2. These fluctuations are inherent to the feeder design and can be as high as ±30% of the average mass flow rate delivered during steady-state operation. This high extent of ceria reduction and CH₄ conversion was realized in very short particle residence times (<1 s) inherent to the present lab-scale reactor. Since complete conversion is thermodynamically favorable at the investigated temperatures. For example, at a methane to ceria ratio of 0.25, complete conversion is favorable at 1000 °C as indicated in Figure 4; thermodynamic limitations were not expected at tube temperatures above 1300 °C. Equilibrium curves for δₑq and X(CH₄)ₑq are indicated in Figure 6a. Figure 6b shows the molar fraction of product species, xᵢ = ̇nᵢ/̇nₗₑq, where ̇nₗₑq corresponds to the sum of all molar flows except Ar but including unmeasured C and H₂O. As expected, both x₇₄ and x₇₃ increased with Tₑq while x₇₁ decreased, yielding at 1350 °C a H₂:CO molar ratio of 2, suitable for gas-to-liquid processing via Fischer–Tropsch. Trace amounts of CO₂ and H₂O were indicative of the high selectivity from CH₄ to syngas. Formation of solid carbon, attributed to CH₄ cracking on hot nucleation surfaces (tube walls and ceria particles), reached a maximum solid phase molar fraction of x₇₄ = 0.13 at 1150 °C but was eliminated at above 1300 °C.

The upgrade factor U is defined as ratio of the energy content in the outlet flow to the energy content of the inlet flow, given by

$$U = \frac{\dot{n}_H HV_H + \dot{n}_CO HV CO + \dot{n}_CeO₂ δ_{fluid} HV CO + \dot{n}_CH₄ HV CH₄}{\dot{n}_CH₄,0 HV CH₄}$$

(4)

where HVᵢ corresponds to the (high) heating value of species i. This definition intrinsically assumes complete reoxidation of ceria with CO₂. Note that the energy content of carbon deposited is not considered because it is an undesirable product. U increased from 0.92 to 1.2 when Tₑq was raised from 1150 °C 1350 °C, as shown in Figure 6c. At Tₑq < 1250 °C, U < 1 partly because of carbon deposition. At Tₑq > 1250 °C, U > 1 which indicates solar energy stored in the form of syngas. For comparison, U < 0.92 for autothermal steam-based reforming of methane without the involvement of ceria, fueled by combustion of excess methane.

Effect of Gas Flow Rate. Figure 7a shows δ_{fluid} and X(CH₄) as a function of the CH₄/Ar gas flow rate while keeping X(CH₄,0) = 0.1, Tₑq = 1300 °C, and ̇m_CeO₂ = 0.14 g s⁻¹ and for the
co-current flow configuration. The corresponding product composition is shown in Figure 7b. With increasing \( V \), the amount of \( \text{CH}_4 \) available for the reaction increased proportionally, resulting in a peak \( \delta_{\text{final}} \) of 0.19 for \( V_{\text{solar}/\text{Ar}} = 3 \text{ L}_N \text{ min}^{-1} \).

A further increase in \( V_{\text{solar}/\text{Ar}} \) resulted in a decrease in \( \delta_{\text{final}} \) and \( x_{\text{CO}} \) due to the carbon formation associated with \( \text{CH}_4 \) cracking, possibly caused by shorter gas and particle residence times and the resulting heat transfer and kinetic limitations. The residence time limitation is further supported by the decrease in \( x_{\text{CH}_4} \) with \( V_{\text{solar}/\text{Ar}} \) shown in Figure 7a. Consequently, \( U \) monotonically decreased as well (Figure 7c).

**Effect of Methane Concentration.** Figure 8a shows \( \delta_{\text{final}} \) and \( x_{\text{CH}_4} \) as a function of \( x_{\text{CH}_4,0} \) for \( T_{\text{tube}} = 1303 \text{ °C}, m_{\text{CeO}_2} = 0.12 \text{ g s}^{-1}, V_{\text{solar}/\text{Ar}} = 2 \text{ L}_N \text{ min}^{-1} \), and co-current flow configuration. The corresponding product compositions are shown in Figure 8b. \( \delta_{\text{final}} \) increased monotonically from 0.088 to 0.18 when \( x_{\text{CH}_4,0} \) increased from 2.5% to 10%, while \( x_{\text{CH}_4} \) remained nearly constant at 0.86 ± 0.02 over this range, corresponding to \( x_{\text{H}_2} = 0.053 \), presumably due to mass transfer effects in the co-current flow configuration. \( x_{\text{H}_2} \) and \( x_{\text{CO}} \) increased with \( x_{\text{CH}_4,0} \) and correlated with a decrease in \( x_{\text{H}_2} \) and \( x_{\text{CO}} \). It is likely, that the particles reach conditions were the reduction with syngas is thermodynamically favorable for low methane to ceria rations, resulting in increased \( \text{H}_2 \) and \( \text{CO} \) formation. Carbon formation was not observed under these conditions, resulting in a constant \( U = 1.25 ± 0.02 \).

**Solar-to-Fuel Energy Conversion Efficiency.** The solar-to-fuel energy conversion efficiency, \( \eta_{\text{solar-to-fuel}} \), is defined as the ratio of the (high) calorific value of syngas (\( \text{H}_2 \) and \( \text{CO} \)) produced to the summation of the solar radiative energy input and the calorific value of the converted \( \text{CH}_4 \). It is thus given by

\[
\eta_{\text{solar-to-fuel}} = \frac{n_{\text{H}_2}HV_{\text{H}_2} + n_{\text{CO}}HV_{\text{CO}} + n_{\text{CeO}_2}HV_{\text{CeO}_2}}{P_{\text{solar}} + (n_{\text{CH}_4,0} - n_{\text{CH}_4})HV_{\text{CH}_4}}
\]

Note that the third term in the numerator accounts for the energy stored in the reduced ceria; i.e., it assumes that reduced ceria is completely reoxidized with \( \text{CO}_2 \) (eq 2a) to generate additional \( \text{CO} \). The heating value of carbon is not included because it is an undesired byproduct. No energy penalty is accounted for inert gas consumption because \( \text{Ar} \) dilution was used only for safety lab regulations.

In contrast, \( m_{\text{CeO}_2} \) had no significant influence regardless of the flow configuration, yielding \( \eta_{\text{solar-to-fuel}} = 8.4 ± 0.4\% \). \( \eta_{\text{solar-to-fuel}} \) increased with \( V \) peaked at 12% for \( V_{\text{solar}/\text{Ar}} = 3 \text{ L}_N \text{ min}^{-1} \) and decreased because of solid carbon deposition and residence time limitations. At this point, it is not possible to compare
these results directly to other studies in the literature. $\eta_{\text{solar-to-fuel}}$ would be a relevant indicator to compare, for example, to the value obtained for the solar reforming of methane without ceria ($\text{CH}_4 + \text{H}_2 \rightarrow 3\text{H}_2 + \text{CO}$). The PNNL’s reforming system, which uses heat exchangers to recover the sensible heat of the hot outlet stream, reports an efficiency of 69% but is defined based on the enthalpy change of the reaction and without considering the calorific value of methane (HV$_{\text{CH}_4}$) as energy input in the denominator, i.e., different definition than eq 5 and thus difficult to compare. Since we are only driving half of the redox cycle without any heat recovery, the particles are heated from ambient to the reaction temperature, affecting detrimentally $\eta_{\text{solar-to-fuel}}$. In a complete cycle with efficient heat management between reduction and oxidation steps, the particles should enter the reactor near the reaction temperature. To maximize $\eta_{\text{solar-to-fuel}}$, the reactor should be operated in the upper range of $T_{\text{tube}}$ while $V_{\text{CH}_4/\text{Ar}}$ needs to be selected to maximize the CH$_4$ supply while avoiding residence time limitations.

**Steady-State Syngas Production.** Figure 10 shows the continuous syngas production for over 60 min for an experimental run with co-current flow configuration and for $T_{\text{tube}} = 1291$ °C, $V_{\text{CH}_4/\text{Ar}} = 2$ L$_N$ min$^{-1}$, $x_{\text{CH}_4,0} = 0.1$, mean $\dot{m}_{\text{CeO}_2} = 0.15$ g s$^{-1}$ ($\dot{n}_{\text{CeO}_2} = 53.7$ mmol min$^{-1}$), co-current flow configuration.

Figure 9. Solar-to-fuel energy conversion efficiency as a function of the nominal temperature of the Al$_2$O$_3$ tube (a), ceria mass flow rate (b), gas flow rate (c), and inlet methane concentration (d). Experimental conditions if not stated otherwise in the graph: $T_{\text{tube}} = 1303$ °C, $\dot{m}_{\text{CeO}_2} = 0.13$ g s$^{-1}$, $V_{\text{CH}_4/\text{Ar}} = 2$ L$_N$ min$^{-1}$, $x_{\text{CH}_4,0} = 0.1$, co-current flow configuration.

Figure 10. Continuous syngas production for over 60 min with stable outlet gas composition. Experimental conditions: $T_{\text{tube}} = 1291$ °C, $\delta = 0.15$, $V_{\text{CH}_4/\text{Ar}} = 2$ L$_N$ min$^{-1}$, $x_{\text{CH}_4,0} = 0.1$, mean $\dot{m}_{\text{CeO}_2} = 0.15$ g s$^{-1}$ ($\dot{n}_{\text{CeO}_2} = 53.7$ mmol min$^{-1}$), co-current flow configuration.
may be avoided by operating at above 1300 °C (Figure 3b) and/or by co-feeding H₂O.

4. SUMMARY AND CONCLUSIONS
The technical feasibility of the solar particle-transport reactor was experimentally demonstrated for performing the combined CeO₂ reduction and CH₄ reforming process using both counter-current and co-current flow configurations. Experiments driven by high-flux irradiation resulted in peak \( \eta_{\text{solar-to-fuel}} \) of 12% and an upgrade factor of 14% at \( T_{\text{tube}} = 1303 \, ^\circ\text{C} \). Molar flow rates of reduced ceria, g s⁻¹, \( \delta \) ceria nonstoichiometry, and methane conversion increased with temperature, while \( i \) = molar fraction of species \( i \). This trend was more pronounced for counter-current and co-current flow configuration. Further, a peak upgrade factor of 24% and methane conversion of 89% were obtained at \( T_{\text{tube}} = 1303 \, ^\circ\text{C} \), with mass flow rate of reduced ceria, g s⁻¹, and \( x_{\text{CH₄}} = 0.1 \) with a co-current flow configuration. Interestingly, H₂ molar fractions decreased with increasing ceria nonstoichiometry, and methane conversion increased with temperature, while carbon formation was suppressed at tube temperatures above 1300 °C. In contrast, nonstoichiometry decreased with increasing ceria mass flow rate, while efficiency and methane conversion were unaffected. Interestingly, H₂ molar fractions decreased with increasing ceria mass flow rate, while the H₂O molar fractions increased correspondingly. This trend was more pronounced for counter-current flow configuration and was attributed to the reaction of unreacted ceria with the produced syngas. Continuous steady-state operation for over 1 h yielded syngas of quality suitable for unreacted ceria with the produced syngas. Continuous steady-state operation for over 1 h yielded syngas of quality suitable for unreacted ceria with the produced syngas.

Ceria nonstoichiometry (reduction extent), efficiency, and methane conversion increased with temperature, while carbon formation was suppressed at tube temperatures above 1300 °C. In contrast, nonstoichiometry decreased with increasing ceria mass flow rate, while efficiency and methane conversion were unaffected.

### NOMENCLATURE DESCRIPTION

| Symbol | Description | Unit |
|--------|-------------|------|
| \( D_{\text{in}} \) | Inner tube diameter | m |
| \( D_{\text{out}} \) | Outer tube diameter | m |
| \( D_{\text{MSO}} \) | Median particle diameter for volume-based distribution, \( \mu \)m |
| \( H \) | Heating value of species \( i \), kJ | |
| \( n \) | Molar ratio of species \( i \) to ceria, mol mol⁻¹ CeO₂⁻¹ |
| \( n_i \) | Molar flow rate of species \( i \), mol s⁻¹ |
| \( \delta \) | Ceria nonstoichiometry at equilibrium |
| \( \eta_{\text{solar-to-fuel}} \) | Solar-to-fuel energy conversion efficiency |

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