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# High-Purity and Clean Syngas and Hydrogen Production From Two-Step CH<sub>4</sub> Reforming and H<sub>2</sub>O Splitting Through Isothermal Ceria Redox Cycle Using Concentrated Sunlight

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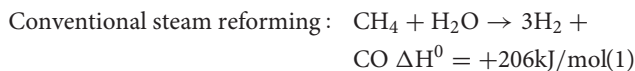
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The thermochemical conversion of methane (CH<sub>4</sub>) and water (H<sub>2</sub>O) to syngas and hydrogen, via chemical looping using concentrated sunlight as a sustainable source of process heat, attracts considerable attention. It is likewise a means of storing intermittent solar energy into chemical fuels. In this study, solar chemical looping reforming of CH<sub>4</sub> and H<sub>2</sub>O splitting over non-stoichiometric ceria (CeO<sub>2</sub>/CeO<sub>2-δ</sub>) redox cycle were experimentally investigated in a volumetric solar reactor prototype. The cycle consists of (i) the endothermic partial oxidation of CH<sub>4</sub> and the simultaneous reduction of ceria and (ii) the subsequent exothermic splitting of H<sub>2</sub>O and the simultaneous oxidation of the reduced ceria under isothermal operation at ~1,000°C, enabling the elimination of sensible heat losses as compared to non-isothermal thermochemical cycles. Ceria-based reticulated porous ceramics with different sintering temperatures (1,000 and 1,400°C) were employed as oxygen carriers and tested with different methane flow rates (0.1–0.4 NL/min) and methane concentrations (50 and 100%). The impacts of operating conditions on the foam-averaged oxygen non-stoichiometry (reduction extent, δ), syngas yield, methane conversion, solar-to-fuel energy conversion efficiency as well as the effects of transient solar conditions were demonstrated and emphasized. As a result, clean syngas was successfully produced with H<sub>2</sub>/CO ratios approaching 2 during the first reduction step, while high-purity H<sub>2</sub> was subsequently generated during the oxidation step. Increasing methane flow rate and CH<sub>4</sub> concentration promoted syngas yields up to 8.51 mmol/g<sub>CeO<sub>2</sub></sub> and δ up to 0.38, at the expense of enhanced methane cracking reaction and reduced CH<sub>4</sub> conversion. Solar-to-fuel energy conversion efficiency, namely, the ratio of the calorific value of produced syngas to the total energy input (solar power and calorific value of converted methane), and CH<sub>4</sub> conversion were achieved in the range of 2.9–5.6% and 40.1–68.5%, respectively.

**Keywords:** methane reforming, ceria foam, redox cycle, concentrated solar power, hydrogen, syngas, H<sub>2</sub>O splitting

## INTRODUCTION

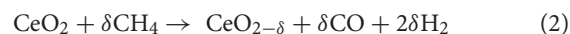
Most hydrogen production is currently achieved via conventional steam reforming of natural gas (Equation 1) (Zheng Q. et al., 2014). The resulting product is syngas ( $H_2+CO$ ), and then water-gas shift reaction is applied to convert the produced CO into  $H_2$  and  $CO_2$ , thus contributing to greenhouse gas emissions. The reaction is endothermic, requiring heat to be supplied to the process for reactions in the temperature range 700–1,000°C (Zheng Q. et al., 2014). In general, the heat source is provided by combustion of up to 41% of the methane feedstock, causing 24% reduction in product energy content compared to the feedstock (Simakov et al., 2015; Krenzke et al., 2017), and costly catalysts are necessary to conduct such reactions (Dincer and Rosen, 2013). This unavoidably results in a significant portion of methane feedstock consumption, as well as greenhouse gas emissions (especially  $CO_2$ ), which contribute to climate change and global warming (Nejat et al., 2015).



Alternatively, the partial oxidation of methane through metal oxide redox cycle (namely, chemical looping reforming of methane, CLRM) is a promising pathway to produce clean syngas and high-purity hydrogen (Di et al., 2019). This reaction encompasses two steps: (1) endothermic partial oxidation of methane along with metal oxide reduction to produce clean syngas and (2) exothermic re-oxidation of the oxide with steam (or  $CO_2$ ) to produce high-purity  $H_2$  (or CO). The net products of CLRM are the same as those of steam reforming (Equation 1). The advantages of CLRM through metal oxides over the conventional methane reforming process are (i) the syngas is produced with a  $H_2:CO$  ratio of 2:1 during the first step, suitable for methanol synthesis (Otsuka et al., 1998), (ii) an excess in oxidizer is not necessary, while a conventional process needs to be operated with excess steam ( $H_2O:CH_4 \geq 3$ ) (Simakov et al., 2015), which raises energy requirements and reduces process efficiency, (iii) catalysts are not required, and (iv) an isothermal operation between both steps is possible; therefore, the temperature swing between the reduction and the oxidation steps can be avoided (Chuayboon et al., 2019a), thereby resulting in fast and continuous process operation (no time wasted for cooling down to oxidation temperature) and lower sensible heat losses, thus improving the energy conversion efficiency. Among a variety of potential metal oxides (either volatile or non-volatile), cerium oxide [either pure ceria (Chueh et al., 2010; Furler et al., 2014; Marxer et al., 2017; Haeussler et al., 2019) or ceria-based (Otsuka et al., 1999; Zheng Y. et al., 2014; Zhu et al., 2014; Bhosale et al., 2019)] is a particularly attractive candidate given its various beneficial physical and chemical properties. For example, ceria keeps a stable cubic fluorite structure during large changes in oxygen non-stoichiometries (reduction extents; Nair and Abanades, 2016) and exhibits rapid oxygen storage/release through lattice transfer (Furler et al., 2014). Marxer et al. (2017) tested the thermochemical splitting of  $CO_2$  using a pure ceria reticulated porous structure and reported that 100% CO

selectivity and 83% molar conversion were achieved. Besides that, 500 consecutive redox cycles were conducted under the same experimental conditions to validate pure ceria stability and structural robustness. A study on the different dopants to ceria (ceria-based ceramics) for two-step thermochemical splitting of  $H_2O/CO_2$  was achieved to improve its stability as well as redox activity (Bhosale et al., 2019). Zhu et al. (2014) studied CLRM over a  $CeO_2-Fe_2O_3$  oxygen carrier and found that this material displayed great performance, thanks to the chemical interaction between Ce and Fe species. The presence of  $CeO_2$ ,  $Fe_3O_4$ , and  $CeFeO_3$  formed in the recycled samples was reported. The reactions of CLRM over ceria include the following steps:

First step: the endothermic reduction reaction of ceria and simultaneous partial oxidation of methane is given in Equation (2).



Second step: the exothermic oxidation reaction of oxygen-deficient ceria with  $H_2O$  is given in Equation (3).



During the reduction step (Equation 2), the amount of released oxygen from ceria ( $\delta_{red}$ ) is calculated by the summation of the mole amounts of CO (main product),  $CO_2$ , and  $H_2O$  according to Equation (4).

$$\delta_{red} = \frac{n_{CO} + 2n_{CO_2} + n_{H_2O}}{n_{CeO_2}} \quad (4)$$

where  $n_i$  is the mole amount of species  $i$ .

During the oxidation step (Equation 3), the amount of oxygen uptake ( $\delta_{ox}$ ) is calculated from the total amount of  $H_2$  produced minus the amount of  $H_2$  produced by the side reactions with respect to the carbon gasification reaction [namely, the carbon produced from methane thermal dissociation,  $CH_4 \rightarrow C + 2H_2$ , during the previous reduction step is gasified with water ( $C + H_2O \rightarrow CO + H_2$  and  $C + 2H_2O \rightarrow CO_2 + 2H_2$ ), producing additional CO,  $CO_2$ , and  $H_2$ ] according to Equation (5).

$$\delta_{ox} = \frac{n_{H_2} - n_{CO} - 2n_{CO_2}}{n_{CeO_2}} \quad (5)$$

To quantify how much injected  $CH_4$  is converted to the products regarding syngas, solid carbon, or soot,  $CH_4$  conversion is calculated by Equation (6).

$$X_{CH_4} = 1 - \frac{\dot{m}_{unreacted\ CH_4}}{\dot{m}_{CH_4}} \quad (6)$$

$X_{CH_4}$  is the methane conversion,  $\dot{m}_{unreacted\ CH_4}$  is the mass flow rate of unreacted methane in the off-gas, and  $\dot{m}_{CH_4}$  is the mass flow rate of injected methane.

The solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ) indicates how well the solar energy is stored into chemical products. It is defined as the ratio of the calorific value of syngas produced by ceria redox cycle to the total energy input, which

is the sum of the calorific value of converted methane and solar power in both the reduction and the oxidation steps, according to Equation (7).

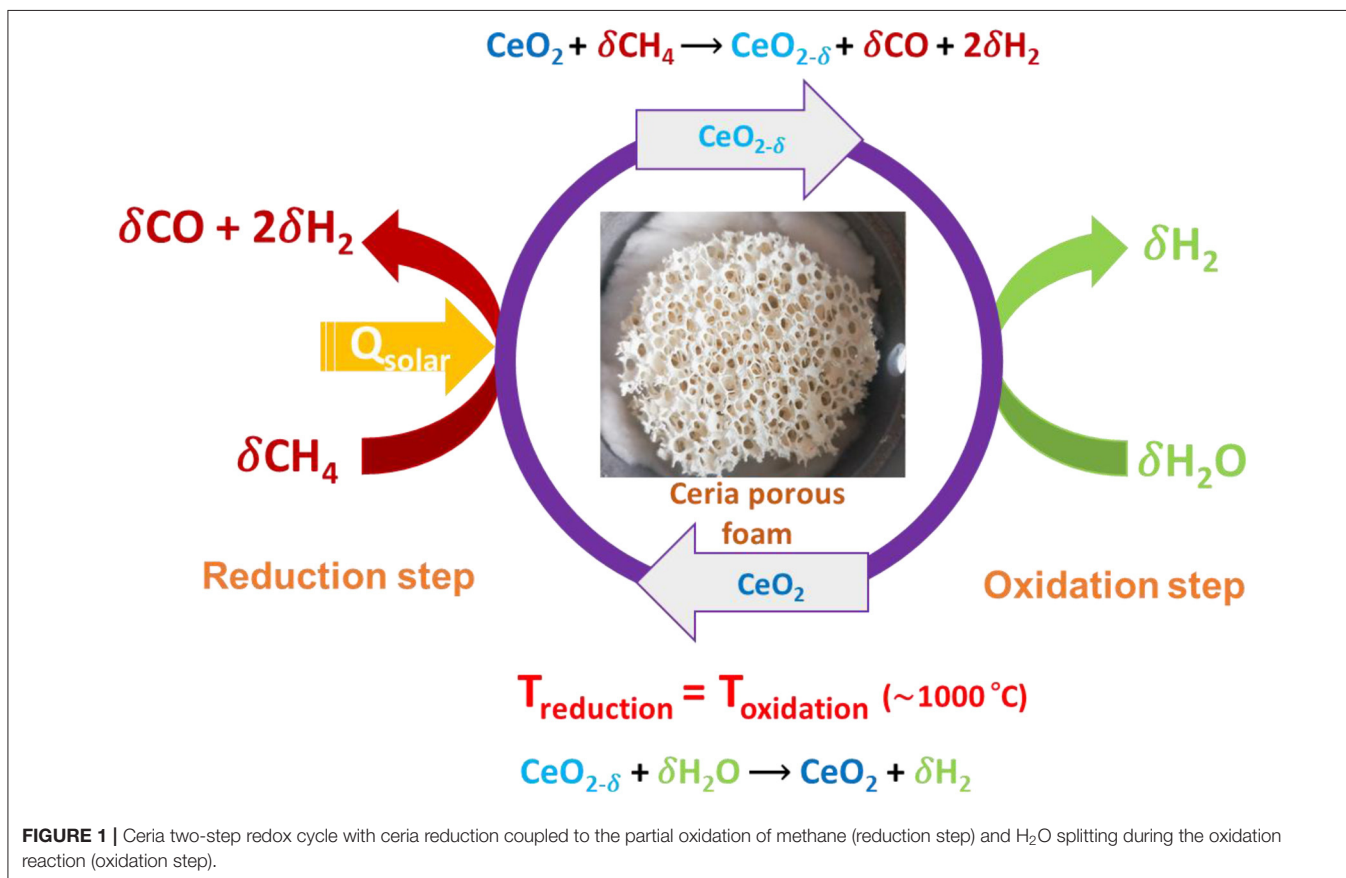
$$\eta_{\text{solar-to-fuel}} = \frac{(\dot{m}_{\text{H}_2} \cdot \text{LHV}_{\text{H}_2} + \dot{m}_{\text{CO}} \cdot \text{LHV}_{\text{CO}})_{\text{cycle}}}{\dot{P}_{\text{solar}} + (X_{\text{CH}_4} \cdot \dot{m}_{\text{CH}_4} \cdot \text{LHV}_{\text{CH}_4})} \quad (7)$$

where  $\text{LHV}_{\text{H}_2}$ ,  $\text{LHV}_{\text{CO}}$ , and  $\text{LHV}_{\text{CH}_4}$  are the lower heating values (J/kg) of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ , respectively,  $\dot{m}_{\text{H}_2}$  and  $\dot{m}_{\text{CO}}$  are the mass flow rates (kg/s) of  $\text{H}_2$  and  $\text{CO}$  produced in the cycle,  $\dot{m}_{\text{CH}_4}$  is the mass flow rate of injected methane, and  $\dot{P}_{\text{solar}}$  is the total solar power input (W).

Otsuka et al. (1993) first conducted partial oxidation of methane with ceria in an electrical furnace at 873–1,073 K, and such reaction was accelerated in the presence of Pt black (1 wt%). As a result, the produced syngas with a  $\text{H}_2/\text{CO}$  ratio of 2 and the reduced ceria oxidation with  $\text{CO}_2$  were demonstrated. They also reported that, in the CLRM process, an excess in oxidizer was not required as carbon deposition can be precluded by limiting the reduction extent of the metal oxides (Otsuka et al., 1999). Then, the processes were coupled with concentrating solar power technologies (Abanades and Flamant, 2006; Chuayboon et al., 2020). The heat required for such endothermic reactions is thus supplied by concentrated sunlight. This offers an attractive approach to convert intermittent solar energy into storable and dispatchable chemical fuels (Nair and Abanades, 2016) as well as

to eliminate  $\text{CO}_2$  emissions from feedstock combustion, thereby offering clean and sustainable fuel production. **Figure 1** presents the concept of two-step solar redox cycle with ceria porous foam reduction coupled to partial oxidation of methane (reduction step) and  $\text{H}_2\text{O}$  splitting during oxidation reaction (oxidation step). Concentrated solar energy is used as the process heat source to drive the endothermic reaction during the reduction step and also to maintain the temperature during the oxidation step for isothermal cycle at  $1,000^\circ\text{C}$  ( $T_{\text{reduction}} = T_{\text{oxidation}}$ ). Furler et al. (2012) reported that ceria-reticulated porous foam enabled the effective volumetric absorption of concentrated sunlight and efficient heat transfer to the whole reacting structure. However, the optical thickness of the porous ceria structure needs to be properly optimized without hindering the specific surface area and density (material loading) since enhancing the latter properties adversely results in high radiative opacity and eventually causes the temperature gradient issue.

Solar CLRM over ceria has been studied both thermodynamically (Krenzke and Davidson, 2014) and experimentally (Welte et al., 2017). Krenzke and Davidson (2014) thermodynamically examined the CLRM with ceria and reported that combining the partial oxidation of methane with ceria allows isothermal cycling at temperatures as low as 1,223 K, with production of high-quality syngas during the reduction step. However, it was found that thermodynamics predicted solar-to-fuel energy conversion efficiency of 40%, significantly



higher than the reported projected ones (e.g., 27%; Krenzke et al., 2016). Then, the same group (Hathaway et al., 2015; Fosheim et al., 2019) studied solar CLRM with CO<sub>2</sub> over ceria in a prototype reactor operated in a high-flux solar simulator. A fixed bed of ceria particles was placed inside six tube assemblies in the reactor. Then, the cycle was carried out by alternating the flow between CH<sub>4</sub> and CO<sub>2</sub>. They reported that a higher temperature favors better performance, and the energetic upgrade factor and the solar-to-fuel energy conversion efficiency were 1.10 and 7%, respectively.

Welte et al. (2017) tested CLRM with ceria particles in a particle transport reactor, either in co-current or counter-current to a CH<sub>4</sub> flow, driven by a solar simulator. Methane conversions up to 89% at 1,300°C for residence times below 1 s and maximum extent of ceria reduction of  $\delta = 0.25$  were mentioned. The solar-to-fuel energy conversion efficiency reached 12%, and the produced syngas was solar-upgraded by 24% compared to feedstock. However, it should be noted that the amount of unreacted ceria exiting the reactor was significant.

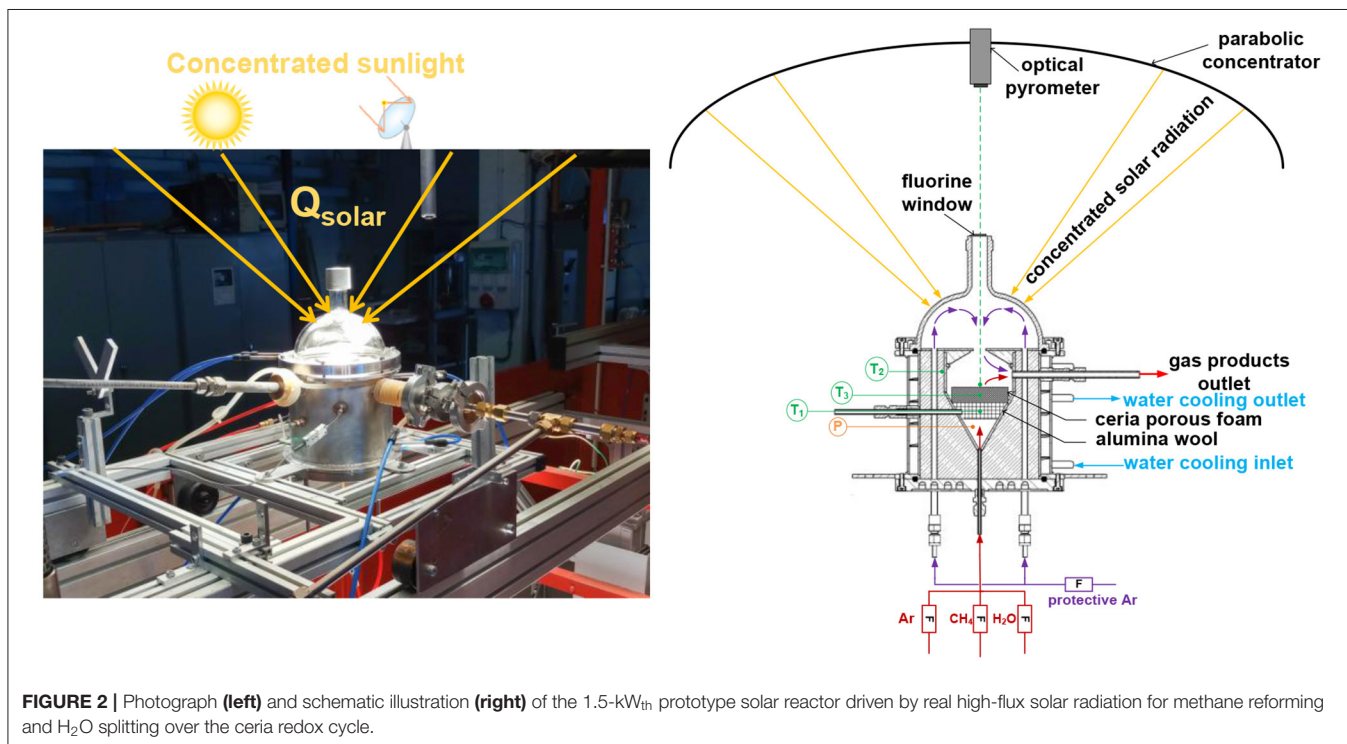
Warren et al. (2017) investigated the cycle thermodynamics in comparison with the experimental investigation of the partial oxidation of methane over ceria. A theoretical solar-to-fuel conversion efficiency over 45% (with no heat recuperation) was claimed, while experimental solar-to-fuel conversion efficiencies of 9.82% (Warren et al., 2017) and later 10.6% (Warren et al., 2020) were obtained in a packed-bed-type solar reactor using solar simulator as heat source. The same research group also explored the kinetics of the partial oxidation of methane over ceria as performed under atmospheric pressure between 750 and 1,100°C using a thermogravimetric analyzer (Warren and Scheffe, 2018, 2019). The reaction kinetics were studied, and

the activation energy was obtained by Arrhenius-type plots as a function of reactant composition. It was found that the activation energy varied with reaction extent between 20 and 80 kJ/mol, rising mostly for large reduction extents ( $\delta > 0.15$ ).

In accordance with prior thermodynamic studies and lab-scale experiments, it was demonstrated that solar CLRM over ceria (as particles or ceramic foam) is of particular interest. However, the reported performance was dependent on the reactor concept, design, and technology. Most of previous studies were likewise focused on thermodynamics (Krenzke and Davidson, 2014; Warren et al., 2017) and experiments (Krenzke et al., 2016; Warren et al., 2020) in small-scale reactors using electrical furnaces or solar simulators as the external heat source instead of real concentrated sunlight. Therefore, this present study aims to further examine the isothermal CLRM and H<sub>2</sub>O splitting over tailor-made ceria porous foams in a scalable prototype solar reactor (1.5 kW<sub>th</sub>) using a real solar concentrating system. The performance of this novel reactor was experimentally assessed, and the impact of transient solar radiation conditions was additionally evaluated. The influence of operating parameters considering CH<sub>4</sub> concentration, methane flow rate, and annealing temperature of ceria foam on thermochemical performance in a 1.5-kW<sub>th</sub> volumetric solar reactor prototype was evaluated and demonstrated.

## MATERIALS AND METHODS

A schematic diagram and a photograph of the 1.5 kW<sub>th</sub> prototype volumetric solar reactor and auxiliary components are presented in **Figure 2**. The solar reactor is heated by



highly concentrated sunlight, delivered by a 2-m-diameter parabolic concentrator with a solar concentration ratio up to 10,551 suns [0.85 m focal distance, peak flux density of  $\sim 10.5 \text{ MW/m}^2$  for a Direct Normal Irradiation (DNI) of  $1 \text{ kW/m}^2$ ] and positioned above the reactor. More details on this solar reactor concept and design have been described previously (Chuayboon et al., 2019b). Three temperature measurements (B-type thermocouples) are installed inside the reactor cavity ( $T_1$  inside alumina wool and  $T_3$  inside ceria porous foam) and at the external cavity wall surface ( $T_2$ ). A solar-blind pyrometer placed at the center of the facedown parabolic concentrator also measures the temperature inside the cavity receiver to compare it with  $T_1$  and  $T_3$ . In addition, one pressure sensor is used to measure the pressure in the reactor cavity ( $P$ ).

Two reactive ceria porous foams were synthesized via replication technique (Furler et al., 2012) using polymer scaffolds as templates, and their physical properties are shown in Table 1. The first ceria foam was annealed at  $1,000^\circ\text{C}$  for 6 h (labeled as CeF-1000), while the other was annealed at  $1,000^\circ\text{C}$  for 6 h and then at  $1,400^\circ\text{C}$  for 2 h (labeled as CeF-1400).

The ceria porous foam was placed on the alumina wool support inside the volumetric ceramic cavity (metallic alloy,

volume: 0.3 L and total height: 115 mm). The reactor was positioned at the focal point of the high flux solar concentrator. It was then heated by concentrated sunlight, while the solar heating rate was adjusted manually using the shutter opening system. Figure 3 shows a representative transient solar power and DNI evolution during both solar heating and isothermal ceria reduction with methane, followed by reduced ceria oxidation with water in the solar reactor (cycle #1, ceria foam CeF-1400, mass 30.963 g). During solar heating (0–45 min), a fluctuation in DNI was evidenced because of transient cloud passage, especially in the morning (10:00–11:00 am). During isothermal ceria reduction with methane, solar power input was adjusted by the shutter to 730 W at  $t = 45\text{--}55 \text{ min}$  (at the beginning of reaction) and increased to 900 W at  $t = 55 \text{ min}$  in order to compensate for the endothermic reaction and solar transients, with the objective to maintain the isothermal operation at  $1,000^\circ\text{C}$ . During oxidation, both solar power input and DNI were quite stable at 900 W and  $1,037 \text{ W/m}^2$  after some transients at the beginning of the period. These variations highlighted the instabilities of real solar power input, which challenged the control of the operating temperature for isothermal operation during on-sun testing.

TABLE 1 | Physical properties of ceria foams.

Number	Annealing temperature ( $^\circ\text{C}$ )	Label	Initial ceria mass (g)	Pore size density (pore per inch)	Specific surface area ( $\text{m}^2/\text{g}$ )	Mean cell size (mm)	Apparent density ( $\text{g}/\text{cm}^3$ )	Apparent porosity (%)
1	1,000	CeF-1000	18.371	10	<1	3.5	0.595	91.8
2	1,400	CeF-1400	30.963	13	<1	2.5	0.780	89.1

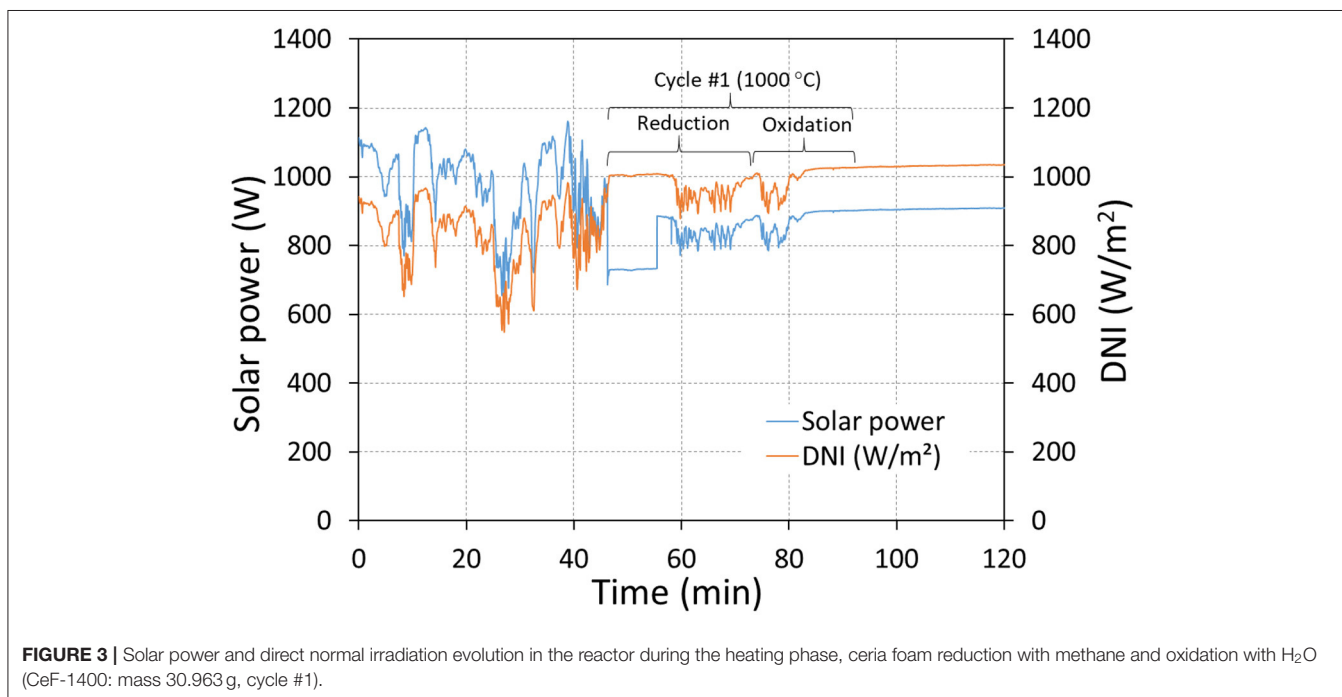


FIGURE 3 | Solar power and direct normal irradiation evolution in the reactor during the heating phase, ceria foam reduction with methane and oxidation with H<sub>2</sub>O (CeF-1400: mass 30.963 g, cycle #1).

**Figure 4** reveals homogeneous temperatures across the ceria-reticulated porous foam, as evidenced by a minimal gap between the top foam surface temperature ( $T_{\text{pyrometer}}$ ), middle temperature ( $T_3$ ), and temperature at the bottom of the foam ( $T_1$ ). In addition, the external cavity wall surface temperature of the reactor cavity receiver ( $T_2$ ) was slightly lower than  $T_{\text{pyrometer}}$ , thereby indicating the uniform solar radiative absorption across the reactive volumetric porous absorber and the solar reactor. This is because the ceria foam exhibits low opacity, while the reactor features high volumetric incident thermal radiation absorption, thus allowing solar energy to penetrate more homogeneously through the foam and reactor cavity receiver. Besides that, the cavity pressure was stable at 0.86 bar during solar heating and rose to 0.90 bar as the reaction progressed ( $P_{\text{atm}} = 0.86$  bar at site elevation). During both steps, the temperatures, especially  $T_3$ , were quite constant at around 1,000°C, demonstrating isothermal operation and satisfying temperature control in case of small DNI variations.

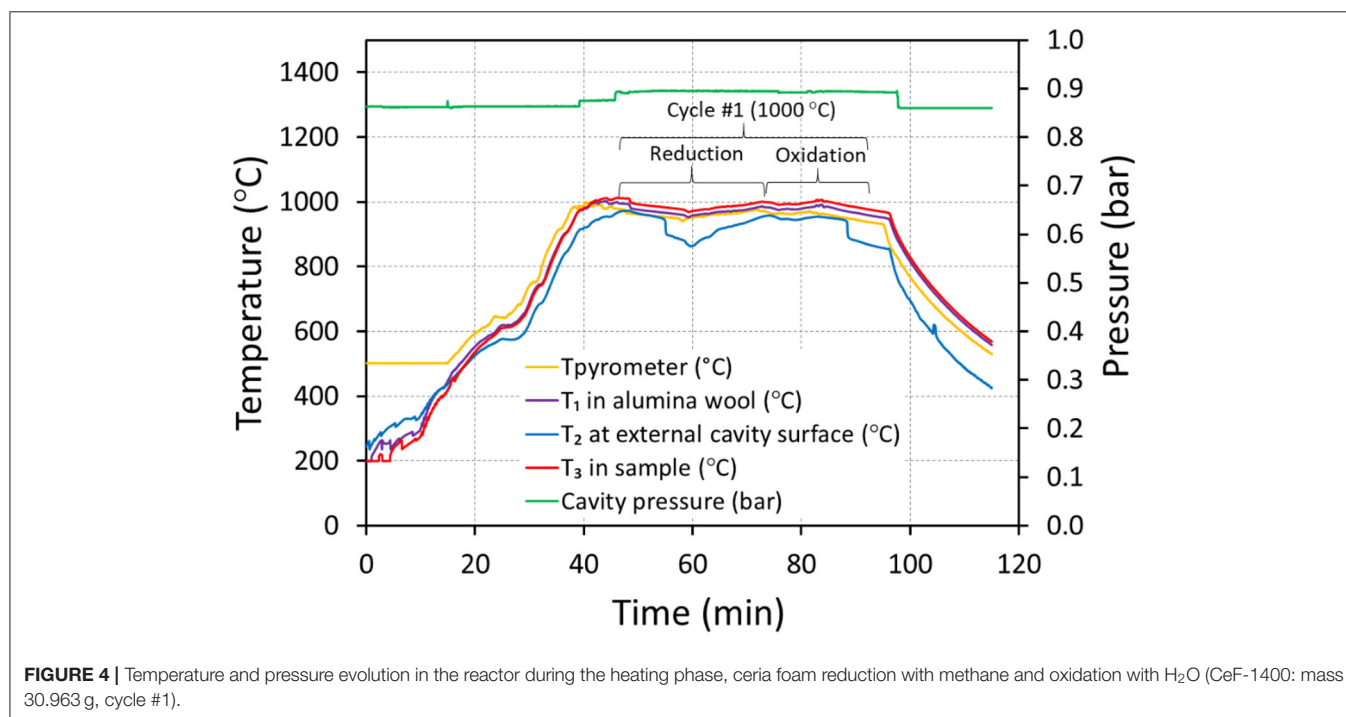
Once the targeted temperature was stabilized at 1,000°C, the CH<sub>4</sub> flow (in the range of 0.1–0.4 NL/min) was introduced along with Ar carrier gas (0.2 NL/min) at the cavity bottom until the reduction reaction was finished. Then, H<sub>2</sub>O (0.2 g/min) was introduced along with Ar carrier gas (0.2 NL/min) for a subsequent oxidation step (liquid water was injected via a stainless steel capillary at the cavity bottom, thanks to a devoted liquid mass flow controller, and was subsequently vaporized when exiting the tube outlet). During reactor heating and reaction proceeding, Ar protective gas flows (2 NL/min) were supplied to protect the transparent window as well as to sweep product gases exiting via the outlet. The produced gases (H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> for methane-promoted redox cycle)

exited the reactor via its outlet port and were then cleaned by both the gas scrubbing system and the filtering unit (in which the H<sub>2</sub>O produced and some soot were trapped) prior to gas analysis. After that, they were continuously analyzed via online gas analyzers (thermal conductivity detector for H<sub>2</sub> and infrared sensors for CO, CO<sub>2</sub>, and CH<sub>4</sub>, calibrated with standard gases). The averaged oxygen non-stoichiometry of CeO<sub>2- $\delta$</sub>  ( $\delta$ ), fuel yields, gas production rates, CH<sub>4</sub> conversion, and solar-to-fuel energy conversion efficiency were experimentally examined and compared. The outlet flow rate of each product gas species ( $F_i$ ) was determined using their measured transient mole fraction ( $y_i$ ) and the known total inlet Ar flow rate ( $F_{\text{Ar}}$ ): ( $F_i = F_{\text{Ar}} \cdot y_i / y_{\text{Ar}}$ ). In addition, the syngas yields from each reaction were calculated separately. For example, the gases produced from the main reactions regarding both partial reduction of ceria by methane (Equation 2) and ceria oxidation (Equation 3) and from the side reactions regarding both the H<sub>2</sub> produced by methane cracking (CH<sub>4</sub> → 2H<sub>2</sub> + C) and the gases produced from C deposit gasification with steam during oxidation (C + H<sub>2</sub>O → CO + H<sub>2</sub> and C + 2H<sub>2</sub>O → CO<sub>2</sub> + 2H<sub>2</sub>) were presented independently in order to highlight the impact of operating conditions on the possible reactions during cycles.

## RESULTS AND DISCUSSION

### Thermodynamic Analysis

**Figure 5** shows the thermodynamic equilibrium composition during the endothermic reduction of ceria and the simultaneous partial oxidation of methane as a function of temperature at 1 bar. With increasing temperature, CH<sub>4</sub> is thermally decomposed to H<sub>2</sub>(g) and solid carbon, and CeO<sub>2</sub> is simultaneously reduced



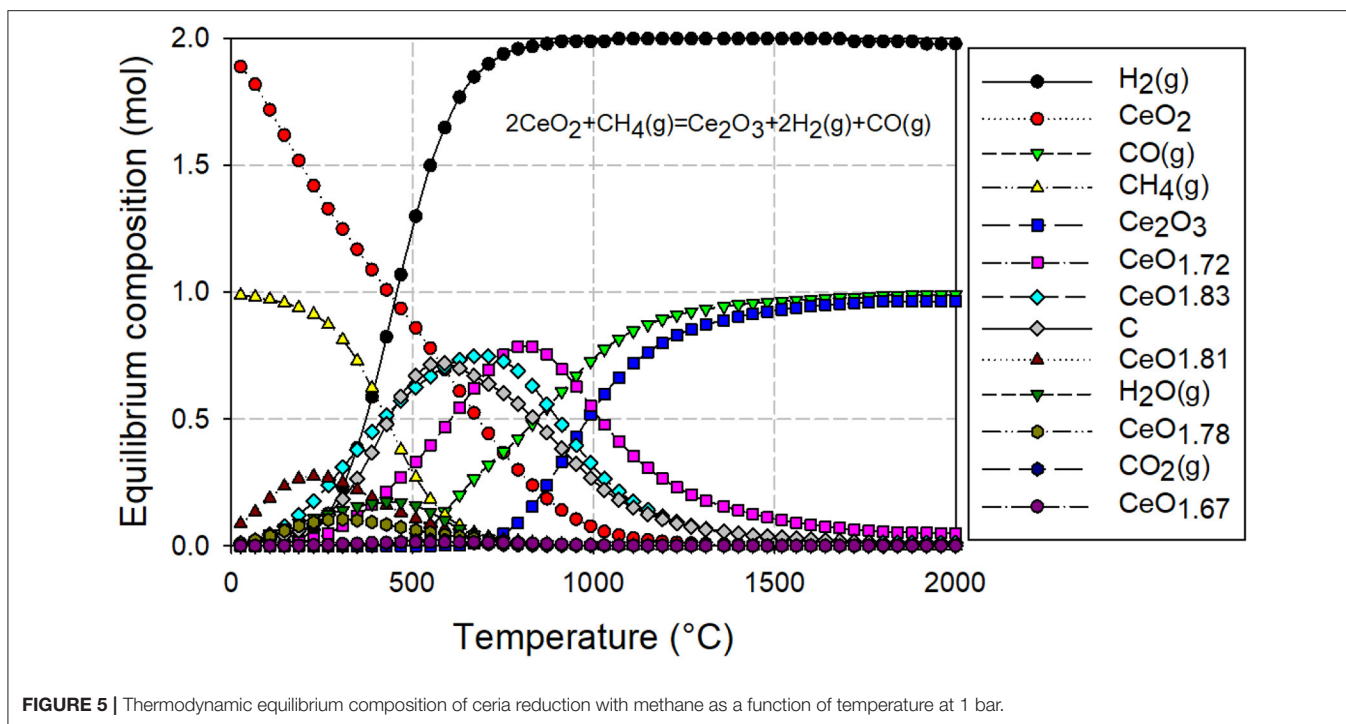


FIGURE 5 | Thermodynamic equilibrium composition of ceria reduction with methane as a function of temperature at 1 bar.

by reactive methane gas (solid–gas reaction), thereby releasing the oxygen from the structure, while partially reduced ceria species ( $\text{CeO}_{1.81}$  and  $\text{CeO}_{1.78}$ ) are formed. Meanwhile, the formation of both  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}_2(\text{g})$  in small amounts is observed. At above  $500^\circ\text{C}$ , the carbon deposition associated with  $\text{CH}_4$  dissociation reacts with the oxygen discharged from ceria, forming  $\text{CO}$  as well as creating the ceria oxygen vacancies, which is in agreement with previous studies (Krenzke and Davidson, 2014; Warren et al., 2017). The intermediate species of ceria regarding  $\text{CeO}_{1.72}$ ,  $\text{CeO}_{1.83}$ , and  $\text{CeO}_{1.67}$  are produced in negligible amounts, demonstrating the overall possible reduction mechanism occurring during  $\text{Ce}(\text{IV})$  reduction to  $\text{Ce}(\text{III})$ . At above  $1,000^\circ\text{C}$ , the completion of the reaction is approached, resulting in  $\text{Ce}_2\text{O}_3$ ,  $\text{H}_2$ , and  $\text{CO}$  (with the  $\text{H}_2/\text{CO}$  ratio approaching 2).

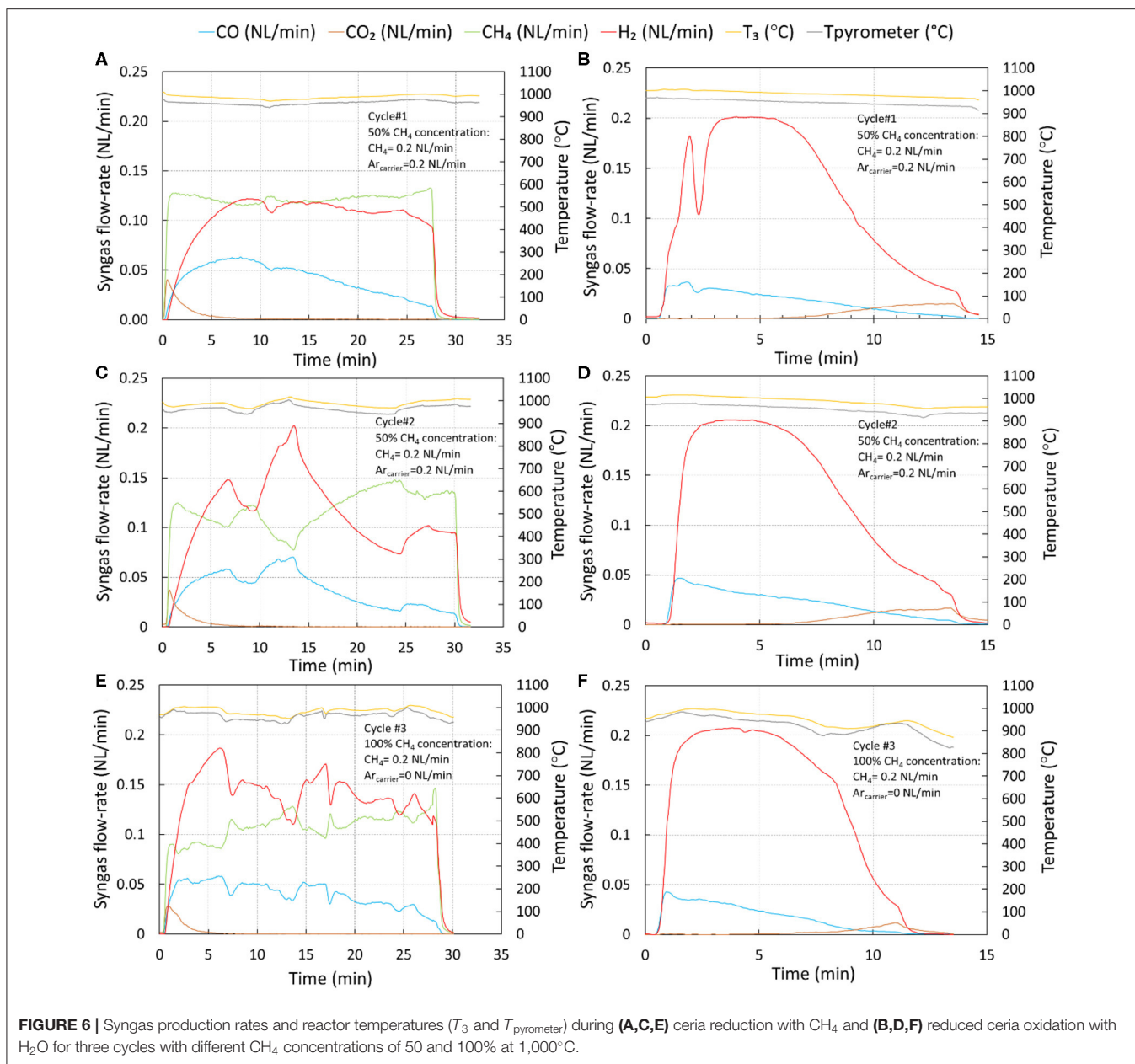
### Effect of Methane Concentration

The effect of methane concentration on syngas production from ceria foam [mass, 30.9630 g; annealed at  $1,400^\circ\text{C}$  (CeF-1400)] was examined for three cycles. Figure 6 shows the evolution of syngas species production rates and temperatures [inside sample ( $T_3$ ) and upper surface sample ( $T_{\text{pyrometer}}$ )] as a function of time during ceria reduction (50%  $\text{CH}_4$  concentration for cycle #1 and cycle #2 and 100%  $\text{CH}_4$  concentration for cycle #3), followed by exothermic ceria oxidation with  $\text{H}_2\text{O}$  (0.2 g/min, 55% steam concentration for three cycles) at the isothermal temperature of  $1,000^\circ\text{C}$ . The variations of the syngas production rates and temperatures provided insights into the chemical reaction behavior and associated mechanism.

At cycle #1 during the reduction step (Figure 6A), a high-quality and energy-rich syngas was produced, with

the  $\text{H}_2/\text{CO}$  molar ratio approaching 2. The maximum of  $\text{CO}_2$  production rate of 0.04 NL/min was evidenced at the initial stage, occurring just after  $\text{CH}_4$  injection. In fact, the  $\text{H}_2\text{O}$  production rate (theoretically doubling the  $\text{CO}_2$  production rate, according to the following reaction:  $4\text{CeO}_2 + \delta\text{CH}_4 \rightarrow 4\text{CeO}_{2-\delta} + \delta\text{CO}_2 + 2\delta\text{H}_2\text{O}$ ) could also be observed according to thermodynamic analysis (Figure 5) and previous studies (Krenzke et al., 2016; Nair and Abanades, 2016). The presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at the initial state of reaction was due to the large amount in the available surface oxygen that reacts with  $\text{CH}_4$  to form both  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . However, the  $\text{H}_2\text{O}$  production rate cannot be measured from gas analysis since the steam was trapped in the gas scrubbing system before the gas analysis. The  $\text{CH}_4$  trend was inverse compared to those of  $\text{H}_2$  and  $\text{CO}$  production rates because of concomitant  $\text{CH}_4$  consumption. After the ceria reduction was completed (depletion of available oxygen inside the ceria structure), the syngas production then decreased progressively. At the end of the reaction,  $\text{CO}$  decreased steadily while  $\text{H}_2$  tended to remain stable, because of the  $\text{CH}_4$  cracking reaction. Indeed when a lack of oxygen occurs at the ceria surface compared to the constant methane feeding rate, carbon deposition is became faster, which is increasingly favored as oxygen is being depleted during the ceria reduction progress. When the  $\text{CO}$  production rate approached zero, the  $\text{CH}_4$  flow was subsequently stopped. During subsequent oxidation (Figure 6B), a sharp increase in  $\text{H}_2$  (0.2 NL/min peak production rate) with high purity was evidenced, thanks to fast oxidation kinetics, followed by  $\text{CO}$  (peak rate, 0.04 NL/min) and  $\text{CO}_2$  (peak rate, 0.02 NL/min) production, which arise from the gasification of carbon deposition (stemming from  $\text{CH}_4$  cracking in the first step).





**FIGURE 6** | Syngas production rates and reactor temperatures ( $T_3$  and  $T_{pyrometer}$ ) during (A,C,E) ceria reduction with  $CH_4$  and (B,D,F) reduced ceria oxidation with  $H_2O$  for three cycles with different  $CH_4$  concentrations of 50 and 100% at  $1,000^\circ C$ .

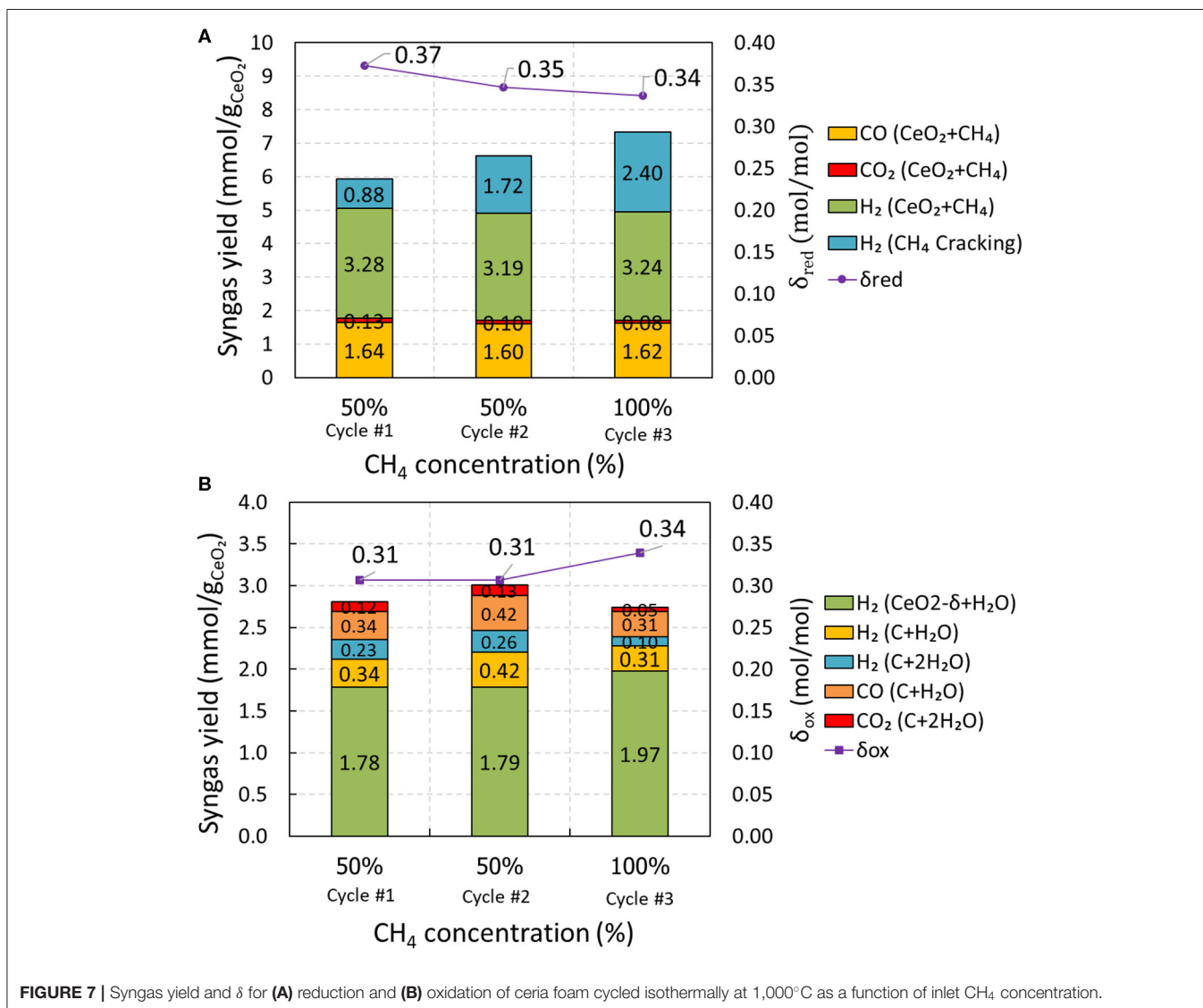
At cycle #2, the experiment was repeated with the same operating parameters as for cycle #1 for both steps. As a result, during reduction (Figure 6C), a fluctuation in syngas and  $CH_4$  flow rates was noticed. This variation can be explained by the fact that the reactor was sometimes heated at above  $1,000^\circ C$  due to the difficulty to control the temperature over 30 min with the manual shutter opening control system, as reflected by  $T_3$  and  $T_{pyrometer}$  fluctuations around the setpoint. As shown in Figure 6C, the trends of  $H_2$  and CO production rates were always consistent with those of the temperatures, demonstrating the strong influence of temperature on ceria reduction reaction. Controlling the operating temperature stably throughout the test is therefore necessary. Moreover, it is important to note that the

peaks of both  $H_2$  and CO were always occurring slightly after the peak of temperature. For example, in Figure 6C, the peak temperature was at 13 min 13 s, while the peaks of  $H_2$  and CO were at 13 min 47 s, which means a 34-s delay, and denoting a small inertia of the reactions. At the final state after a 25-min duration, a plateau region in syngas and  $CH_4$  evolution was evidenced due to the thermally favorable  $CH_4$  cracking reaction caused by solar overheating ( $>1,000^\circ C$ ). During the oxidation step (Figure 6D), the  $H_2$  peak production rate increased up to 0.21 NL/min, while the CO and  $CO_2$  peak production rates were 0.05 and 0.02 NL/min, thus slightly higher than those measured in cycle #1, confirming the stronger effect of  $CH_4$  cracking reaction during the reduction step.

At cycle #3 during reduction (**Figure 6E**), CH<sub>4</sub> concentration was increased to 100% (CH<sub>4</sub> flow rate = 0.2 NL/min without Ar carrier gas at the bottom inlet). Similar to the previous cycle, the syngas and CH<sub>4</sub> production rates still varied in relation to a change in temperature, implying a significant temperature effect on possible reactions. The difference of syngas production rate between 50% (cycle #2) and 100% (cycle #3) methane concentration was not obvious. However, H<sub>2</sub> trend seemed to be higher, while CO trend seemed to be similar as compared to those obtained from cycle #2. In addition, the nominal gas residence time (calculated from the volume of the cavity divided by the total outlet gas flow rate) was 1.87 s at 100% CH<sub>4</sub> concentration compared to 1.70 s at 50% CH<sub>4</sub> concentration, which may in turn promote CLRM over ceria. During oxidation (**Figure 6F**), the peak H<sub>2</sub> production rate was found to be the same as in cycle #2 (0.21 NL/min), but the peak CO (0.04 NL/min) and CO<sub>2</sub> (0.01 NL/min) production rates were lower compared to those in cycle #2, possibly because of a decline in temperature after a 5-min

duration (below 1,000°C), which lowers the endothermic carbon gasification reactions (C + H<sub>2</sub>O → CO + H<sub>2</sub>). This might lead to solid carbon remaining inside the reactor cavity receiver.

**Figure 7** presents the syngas yields during the (a) reduction and the (b) oxidation steps, quantified by time integration of the syngas production rates according to **Figure 6**. During the reduction step at 50% of CH<sub>4</sub> concentration (**Figure 7A**), the H<sub>2</sub> yield (from CH<sub>4</sub> cracking) from cycle #2 was considerably higher [1.72 (cycle #2) vs. 0.88 mmol/gCeO<sub>2</sub> (cycle #1)], thus confirming increased thermal CH<sub>4</sub> decomposition due to overheating as mentioned before. In contrast, the CO<sub>2</sub> yield was lower [0.13 mmol/gCeO<sub>2</sub> (cycle #1) vs. 0.10 mmol/gCeO<sub>2</sub> (cycle #2)], which is attributed to the fresh ceria foam that released more oxygen, as reflected by the highest δ<sub>red</sub> (0.37). Besides that, both H<sub>2</sub> (from CeO<sub>2</sub> + CH<sub>4</sub>) and CO (from CeO<sub>2</sub> + CH<sub>4</sub>) yields remained similar between cycle #1 and cycle #2, demonstrating syngas production yield repeatability. When increasing the CH<sub>4</sub> concentration to 100% (cycle #3), a significant increase



**FIGURE 7** | Syngas yield and  $\delta$  for (A) reduction and (B) oxidation of ceria foam cycled isothermally at 1,000°C as a function of inlet CH<sub>4</sub> concentration.

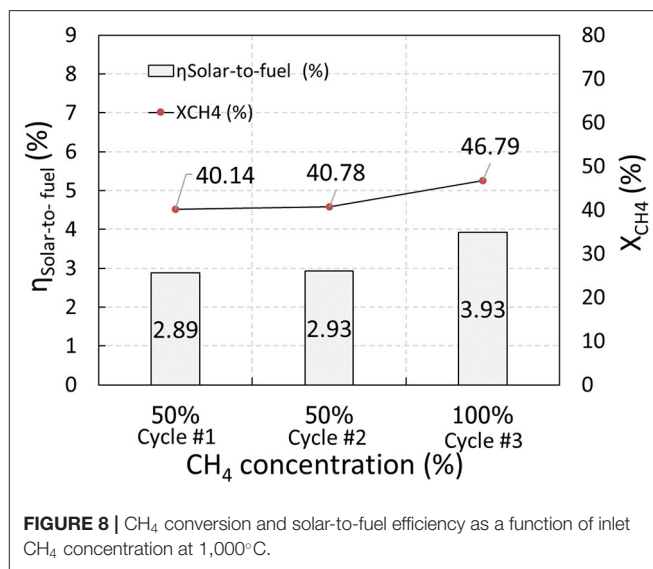
in H<sub>2</sub>, associated with CH<sub>4</sub> cracking, was evidenced (2.40 mmol/g<sub>CeO<sub>2</sub></sub>), presumably due to both overheating and higher CH<sub>4</sub> concentration. Furthermore, at 100% CH<sub>4</sub> concentration (cycle #3), a small increase in CO (CeO<sub>2</sub> + CH<sub>4</sub>) and H<sub>2</sub> (CeO<sub>2</sub> + CH<sub>4</sub>) yields was noticed when compared to 50% CH<sub>4</sub> concentration (cycle #2), demonstrating a positive impact on the main reaction. A slight change in CO (CeO<sub>2</sub> + CH<sub>4</sub>) and CO<sub>2</sub> (CeO<sub>2</sub> + CH<sub>4</sub>) yields led to similar  $\delta_{red}$  (0.35 at cycle #2 vs. 0.34 at cycle #3). Therefore, increasing the CH<sub>4</sub> concentration may favor both the main reaction (CeO<sub>2</sub> + CH<sub>4</sub>), as reflected by the improvement of CO (from CeO<sub>2</sub> + CH<sub>4</sub>) and H<sub>2</sub> (from CeO<sub>2</sub> + CH<sub>4</sub>) yields along with the side reaction (CH<sub>4</sub> cracking) as reflected by H<sub>2</sub> (from CH<sub>4</sub> cracking).

During the oxidation step (Figure 7B) at 50% CH<sub>4</sub> concentration, H<sub>2</sub> (C + H<sub>2</sub>O), H<sub>2</sub> (C + 2H<sub>2</sub>O), CO (C + H<sub>2</sub>O), and CO<sub>2</sub> (C + 2H<sub>2</sub>O) yields at cycle #2 were found to be higher than those from cycle #1 as expected, confirming a higher carbon deposition amount obtained during the reduction step, which was oxidized with H<sub>2</sub>O. Besides that, the H<sub>2</sub> yield associated with the main reaction (CeO<sub>2- $\delta$</sub>  + H<sub>2</sub>O) was stable [1.79 mmol/g<sub>CeO<sub>2</sub></sub> (cycle #2) vs. 1.78 mmol/g<sub>CeO<sub>2</sub></sub> (cycle #1)], leading to the same value of  $\delta_{ox}$  (0.31). Importantly, the H<sub>2</sub> (C + H<sub>2</sub>O), H<sub>2</sub> (C + 2H<sub>2</sub>O), CO (C + H<sub>2</sub>O), and CO<sub>2</sub> (C + 2H<sub>2</sub>O) yields at cycle #3 were lower compared to those from cycle #2 even though the H<sub>2</sub> (cracking) yield was higher (Figure 7A). This is because of the decline of the oxidation temperature (below 1,000°C) that decreased the carbon deposition gasification reaction, leading to lower H<sub>2</sub> (C + H<sub>2</sub>O), H<sub>2</sub> (C + 2H<sub>2</sub>O), CO (C + H<sub>2</sub>O), and CO<sub>2</sub> (C + 2H<sub>2</sub>O) yields. On the other hand, a drop in the temperature during the oxidation step (cycle #3) positively influenced the exothermic reduced ceria oxidation with H<sub>2</sub>O, leading to a higher H<sub>2</sub> (CeO<sub>2- $\delta$</sub>  + H<sub>2</sub>O) yield (1.97 mmol/g<sub>CeO<sub>2</sub></sub>). Moreover, at cycle #3,  $\delta_{red}$  (0.34) exactly matched  $\delta_{ox}$  (0.34), confirming a complete oxidation.

Figure 8 represents CH<sub>4</sub> conversion ( $X_{CH_4}$ ) and solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ) for the three cycles at different CH<sub>4</sub> concentrations. As expected, the highest  $X_{CH_4}$  was found at cycle #3 (46.79%) due to the higher impact of CH<sub>4</sub> concentration and CH<sub>4</sub> cracking reaction, followed by cycle #2 (40.78%) and cycle #1 (40.14%), in agreement with the trend of the syngas yield (Figure 7A). The  $\eta_{solar-to-fuel}$  rose slightly with CH<sub>4</sub> concentration and exhibited the maximum (3.93%) at cycle #3. It was quite low as the solar power input was taken into account for both steps, including the duration of the reactor purging with Ar flow before switching to the oxidation step.

### Effect of Methane Flow Rate

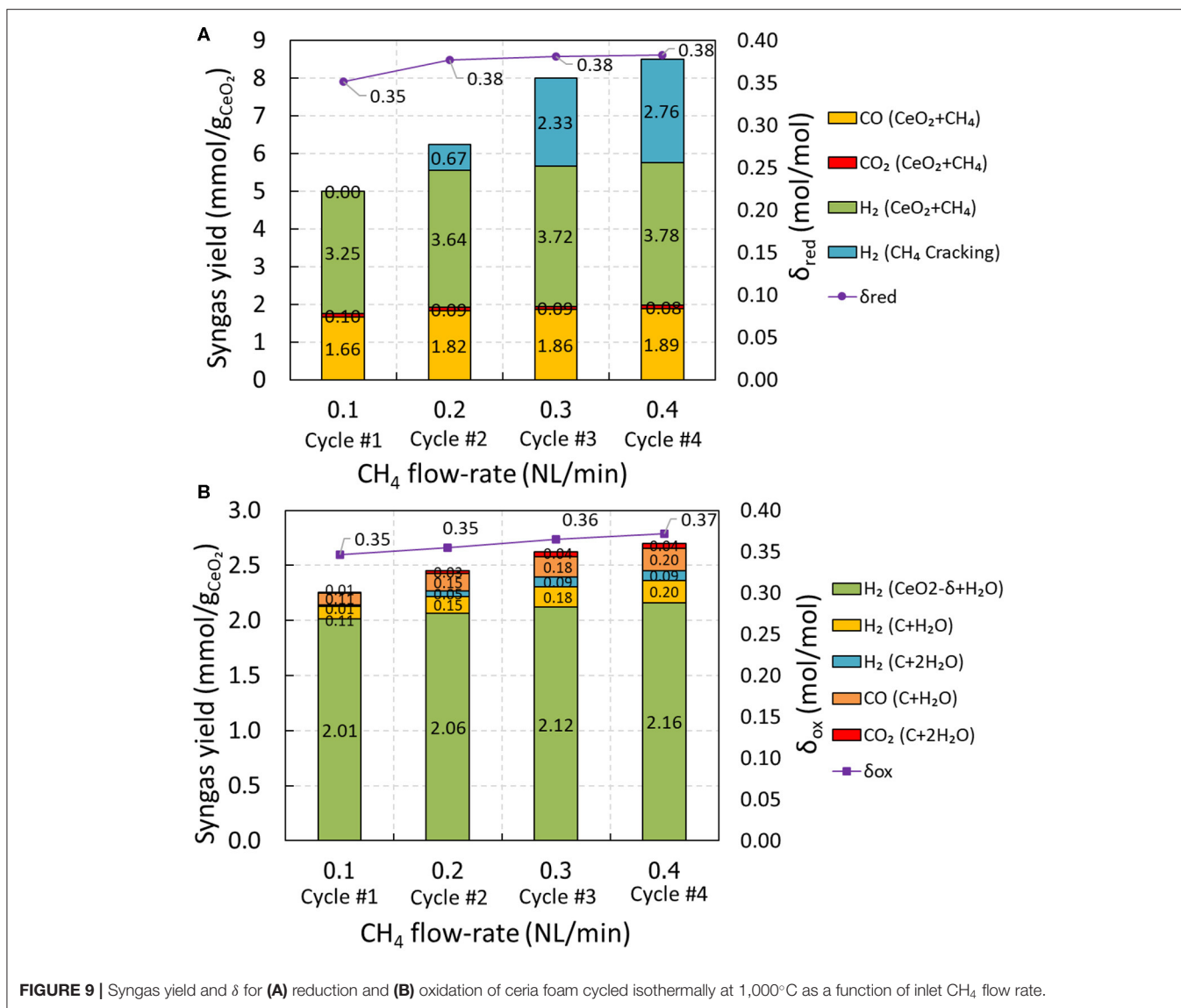
The impact of methane flow rate on syngas production from ceria foam [mass, 18.371g; annealed at 1,000°C (CeF-1000)] was studied for four cycles. Figure 9 shows the influence of methane flow rate on the resulting syngas yields during ceria reduction with methane (Figure 9A), followed by ceria oxidation with H<sub>2</sub>O (Figure 9B). The CH<sub>4</sub> flow rate was adjusted at 0.1, 0.2, 0.3, and 0.4 NL/min, together with a constant Ar carrier gas flow of 0.2 NL/min injected from the bottom inlet,



resulting in CH<sub>4</sub> concentrations of 33.3, 50, 60, and 66.6% in the bottom gas flow.

During the reduction step (Figure 9A), the H<sub>2</sub> (CeO<sub>2</sub> + CH<sub>4</sub>) and CO (CeO<sub>2</sub> + CH<sub>4</sub>) yields increased moderately with CH<sub>4</sub> flow rate, from 3.25 and 1.66 mmol/g<sub>CeO<sub>2</sub></sub> at 0.1 NL/min to 3.78 and 1.89 mmol/g<sub>CeO<sub>2</sub></sub> at 0.4 NL/min, respectively, thereby enhancing the  $\delta_{red}$  from 0.35 to 0.38. The CO<sub>2</sub> (CeO<sub>2</sub> + CH<sub>4</sub>) yield was found to be stable in the range 0.08–0.10 mmol/g<sub>CeO<sub>2</sub></sub>. Importantly, a sharp rise in the H<sub>2</sub> (CH<sub>4</sub> cracking) yield with CH<sub>4</sub> flow rate was observed, increasing from 0 at 0.1 NL/min (denoting the absence of the CH<sub>4</sub> cracking reaction) to 2.76 mmol/g<sub>CeO<sub>2</sub></sub> at 0.4 NL/min. This can be explained by the fact that the ceria reduction approached completion when the inlet CH<sub>4</sub> flow rate was increased, as reflected by  $\delta_{red}$  that tended to level off at 0.38 above 0.2 NL/min. For these reasons, the rate of CH<sub>4</sub> supply exceeded the rate of oxygen released from the ceria structure, thereby leading to a favorable CH<sub>4</sub> cracking reaction. These phenomena usually happen when the rate of diffusion of the bulk lattice oxygen to the ceria surface is slower than methane dissociation, which leads to chemisorbed carbon being accumulated on the surface. In addition, the growth in the H<sub>2</sub> (CH<sub>4</sub> cracking) yield with CH<sub>4</sub> flow rate was in agreement with the growth of H<sub>2</sub> (CH<sub>4</sub> cracking) yield with CH<sub>4</sub> concentration, confirming that an increasing CH<sub>4</sub> concentration has an influence on CH<sub>4</sub> cracking reaction (Figure 7A).

During the oxidation step (Figure 9B), as expected the H<sub>2</sub> (CeO<sub>2- $\delta$</sub>  + H<sub>2</sub>O) yield associated with the main reaction rose constantly with CH<sub>4</sub> flow rate, from 2.01 at 0.1 NL/min to 2.16 mmol/g<sub>CeO<sub>2</sub></sub> at 0.4 NL/min. This is due to the enhancement of the reduction extent during the reduction step that increased the oxygen vacancies. Consequently, the  $\delta_{ox}$  was improved in the range 0.35–0.37 mol<sub>O</sub>/mol<sub>CeO<sub>2</sub></sub>. Regarding the resulting syngas yields associated with the side reactions, the H<sub>2</sub> (C + H<sub>2</sub>O), H<sub>2</sub> (C + 2H<sub>2</sub>O), CO (C + H<sub>2</sub>O), and CO<sub>2</sub> (C + 2H<sub>2</sub>O) yields increased with increasing CH<sub>4</sub> flow rate during the reduction step, from 0.01, 0.11, 0.01, and 0.11 mmol/g<sub>CeO<sub>2</sub></sub> at 0.1 NL/min to



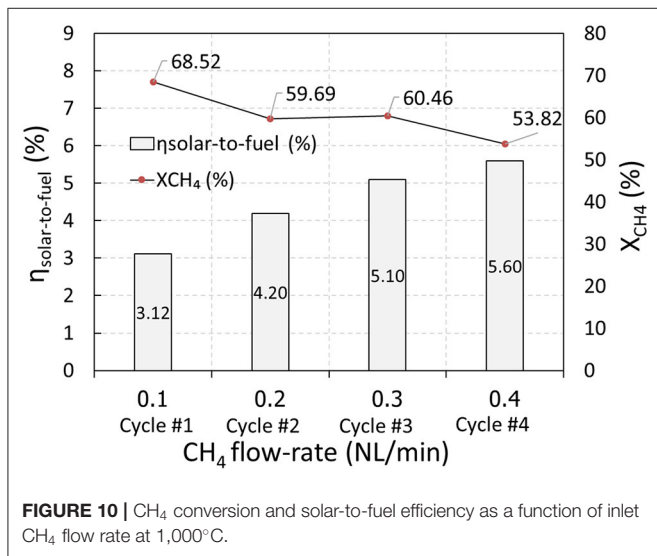
**FIGURE 9** | Syngas yield and  $\delta$  for (A) reduction and (B) oxidation of ceria foam cycled isothermally at 1,000°C as a function of inlet CH<sub>4</sub> flow rate.

0.04, 0.20, 0.09, and 0.20 mmol/gCeO<sub>2</sub> at 0.4 NL/min, respectively. This is attributed to the growth of solid carbon deposition caused by CH<sub>4</sub> dissociation with the increase of the CH<sub>4</sub> flow rate. However, this carbon can be gasified with H<sub>2</sub>O, thus avoiding the issue of carbon remaining inside the reactor cavity receiver. For these reasons, increasing the methane flow rate enhances the extent of reaction and syngas yield; however, an excessive increase in the methane flow rate has a negative impact by increasing CH<sub>4</sub> dissociation, which results in the formation of CO and CO<sub>2</sub> during the oxidation step, thereby downgrading the H<sub>2</sub> purity.

The  $\delta_{red}$  and  $\delta_{ox}$  values were likewise similar for each tested CH<sub>4</sub> flow rate, indicating that the amount of oxygen being released and reversibly recovered is identical, thus again confirming complete reduced ceria re-oxidation with H<sub>2</sub>O.

As expected, X<sub>CH<sub>4</sub></sub> declined with increasing CH<sub>4</sub> flow rate, from 68.52% at 0.1 NL/min to 53.82% at 0.4 NL/min, according to **Figure 10**. This is because the rate of CH<sub>4</sub> supply was higher

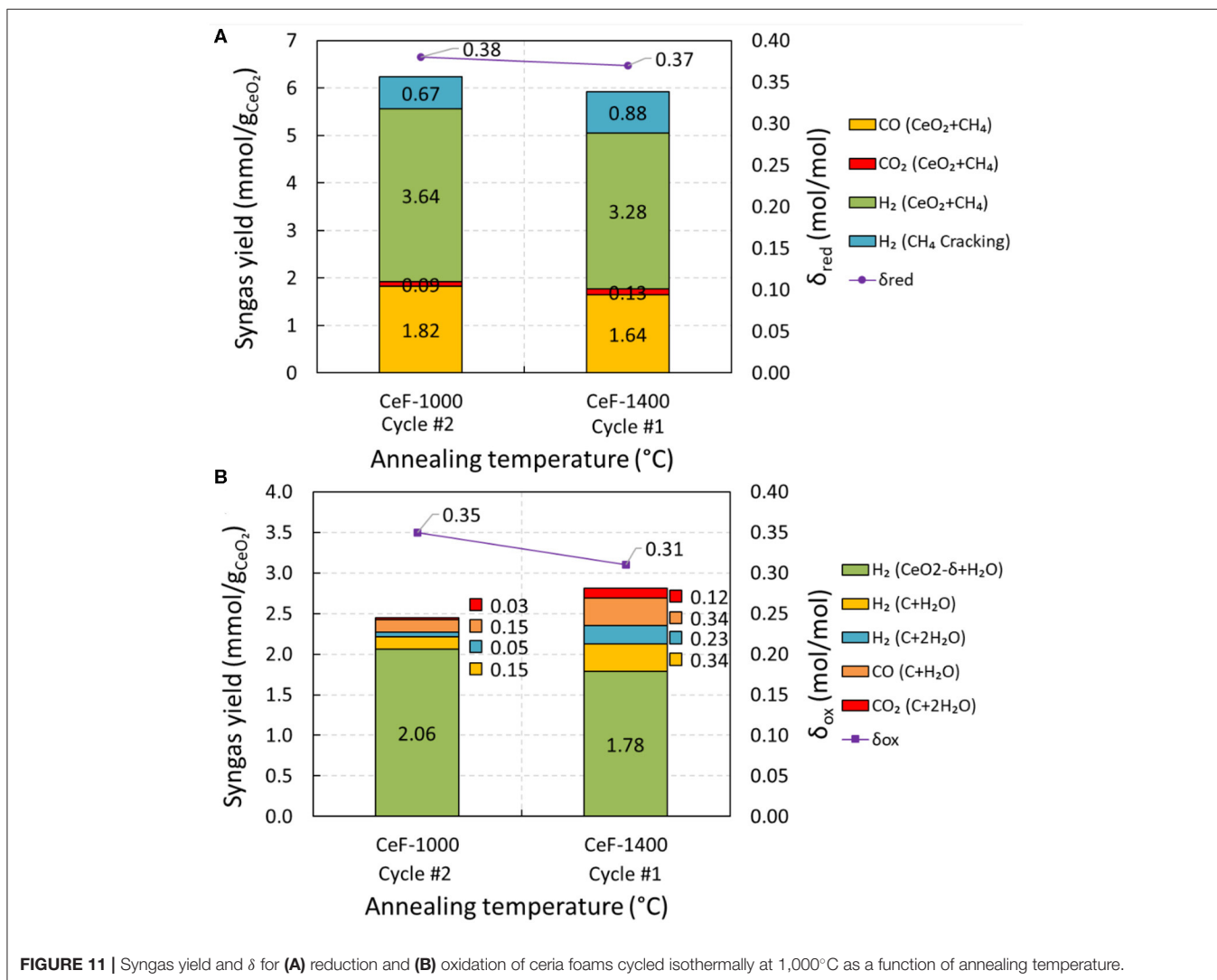
than the rate of oxygen discharged by ceria reduction reaction. The X<sub>CH<sub>4</sub></sub> values reported here were comparable with those of previous studies [16–44% (Warren et al., 2020) and 13–60% (Krenzke et al., 2016)]. In addition, X<sub>CH<sub>4</sub></sub> was found to be dependent on the inlet methane flow rate. This is related to the methane cracking reaction, which resulted in solid carbon deposition. Therefore, an optimal trade-off in the inlet methane flow rate needs to be considered to maximize the methane conversion, which results in high syngas yield while minimizing the methane cracking side reaction. The  $\eta_{solar-to-fuel}$  rose with the CH<sub>4</sub> flow rate and reached 5.6% at 0.4 NL/min, thanks to the improvement of the syngas yield with the CH<sub>4</sub> flow rate, as evidenced by **Figure 9**. The obtained  $\eta_{solar-to-fuel}$  values were found to be typical with respect to the lab-scale solar reactors and comparable to previous studies (Warren et al., 2017; Fosheim et al., 2019). It is usual that the  $\eta_{solar-to-fuel}$  values are lower than the theoretical ones predicted by thermodynamic



analysis (Warren et al., 2017). The  $\eta_{\text{solar-to-fuel}}$  can be potentially enhanced by scaling up the reactors to reduce heat losses, by optimizing heat and mass transfer inside the reactor and porous medium to improve the reaction rates and shorten the cycle duration (thereby lowering solar energy input), and by operating the process at optimal conditions to maximize the conversion of CH<sub>4</sub> and H<sub>2</sub>O.

### Influence of Ceria Annealing Temperature

The effect of annealing temperatures (1,000 vs. 1,400°C) of ceria foam on syngas yield was examined at a constant CH<sub>4</sub> flow rate of 0.2 NL/min with 50% CH<sub>4</sub> concentration during the reduction step and subsequently at a constant H<sub>2</sub>O flow rate of 0.2 g/min with 55% H<sub>2</sub>O concentration during the oxidation step. The syngas yield obtained from cycle #2 (CeF-1000) was compared to that obtained from cycle #1 (CeF-1400), as presented in **Figure 11**. It was found that during the reduction step (**Figure 11A**), the ceria foam CeF-1400 showed lower H<sub>2</sub> (CeO<sub>2</sub> + CH<sub>4</sub>) and CO (CeO<sub>2</sub> + CH<sub>4</sub>) yields than those for



CeF-1000, in turn resulting in a lower  $\delta_{\text{red}}$  (0.37). Actually, the increasing annealing temperature (CeF-1400) resulted in the high densification of the ceria structure as evidenced by a decrease in density as well as porosity (Table 1), thereby leading to lower reduction extent and syngas yield. However,  $\text{H}_2$  ( $\text{CH}_4$  cracking) for CeF-1400 was higher (0.67 mmol/g $_{\text{CeO}_2}$  for CeF-1000 vs. 0.88 mmol/g $_{\text{CeO}_2}$  for CeF-1400). This is basically attributed to the longer reduction reaction duration for CeF-1400 (10-min duration for ceria mass 18.371 g of CeF-1000 vs. 30-min duration for ceria mass 30.963 g of CeF-1400), which provides an extended duration for the  $\text{CH}_4$  cracking reaction to proceed.

Figure 11B, which is related to oxidation step, confirmed that the influence of  $\text{CH}_4$  cracking reaction for CeF-1400 was higher when compared to CeF-1000, as evidenced by higher  $\text{H}_2$  ( $\text{C} + \text{H}_2\text{O}$ ),  $\text{H}_2$  ( $\text{C} + 2\text{H}_2\text{O}$ ),  $\text{CO}$  ( $\text{C} + \text{H}_2\text{O}$ ), and  $\text{CO}_2$  ( $\text{C} + 2\text{H}_2\text{O}$ ) yields associated with the steam gasification of carbon. As expected, an increase in the annealing temperature significantly lowered the  $\text{H}_2$  ( $\text{CeO}_{2-\delta} + \text{H}_2\text{O}$ ) yield associated with steam ceria oxidation (e.g., from 2.06 mmol/g $_{\text{CeO}_2}$  for CeF-1000 to 1.78 mmol/g $_{\text{CeO}_2}$  for CeF-1400, in turn decreasing  $\delta_{\text{ox}}$  from 0.35 to 0.31). For these reasons, it can be summarized that the annealing temperature of ceria foam should be as low as possible in order to increase its porosity, which promotes solid–gas reactions, thereby enhancing the reaction extent.

## CONCLUSIONS

Chemical looping reforming of methane and  $\text{H}_2\text{O}$  splitting from isothermal ceria redox cycle for efficient syngas and hydrogen production have been assessed thermodynamically and experimentally. A 1.5-kW $_{\text{th}}$  prototype volumetric reactor has been operated with real solar concentrated energy under isothermal conditions at 1,000°C, thereby demonstrating the technical feasibility and the reliability of the innovative and ecofriendly solar-driven methane reforming system for producing clean fuels. A parametric study considering the influence of inlet  $\text{CH}_4$  concentration,  $\text{CH}_4$  flow rate, and annealing temperature on syngas production rate, yield, foam-averaged oxygen non-stoichiometry ( $\delta$ ),  $\text{CH}_4$  conversion, and reactor performance was performed. In agreement with thermodynamic predictions, syngas yield was produced with

$\text{H}_2/\text{CO}$  ratios approaching 2, along with undesired products regarding  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at the initial state of the reduction reaction. Increasing  $\text{CH}_4$  concentration (50 and 100%) and  $\text{CH}_4$  flow rate (0.1–0.4 NL/min) enhanced the reduction extent and syngas and hydrogen production yields during both steps, at the expense of a favorable  $\text{CH}_4$  cracking reaction, which formed solid carbon deposition. However, the solid carbon is not detrimental to the whole process because carbon can be gasified with  $\text{H}_2\text{O}$  in the oxidation step (although producing  $\text{CO}$  and  $\text{CO}_2$  and thus impacting the  $\text{H}_2$  purity). In addition, a compromise temperature during the oxidation step should be considered, favoring exothermic reduced ceria oxidation while ensuring endothermic carbon deposition gasification with  $\text{H}_2\text{O}$ . Moreover, the sensitivity of the process to the temperature during on-sun testing was found to be significant, demonstrating that the transient conditions of a real solar-driven process need to be considered in scaling up the process. Increasing the annealing temperature of ceria foam had an adverse impact on its physical properties regarding density and porosity, leading to a decrease in the reduction extent and the syngas yield. Finally, solar-to-fuel conversion efficiency was in the range 2.9–5.6%, while  $\text{CH}_4$  conversion in the range of 40.2–68.5% was achieved. Future work will aim at performing this process using renewable gaseous feedstocks such as biomethane, biogas, as well as biohythane for purely renewable (and carbon-neutral) fuel production.

## DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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