

# Improving solar fuel production performance from H2O and CO2 thermochemical dissociation using custom-made reticulated porous ceria

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1	Improving solar fuel production performance from H <sub>2</sub> O and CO <sub>2</sub>
2	thermochemical dissociation using custom-made reticulated porous
3	ceria
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12	
13	Abstract
14	Thermochemical $CO_2$ - and $H_2O$ -splitting cycles for sustainable fuel generation were investigated by
15	using custom-made reticulated ceria foams integrated in a solar-heated cavity reactor. A parametric
16	study revealed the suitable conditions to produce $H_2/CO$ with maximum fuel rates and yields per unit
17	mass of redox material. Various operating parameters such as the total pressure during the reduction
18	step, the gas inlet flowrates, the temperature or the reactive gas content during the oxidation step
19	were studied in detail. A series of on-sun experiments including more than 20 cycles under different
20	cycling conditions were carried out with relevant performance repeatability and stability. With a ceria
21	foam reduction temperature in the range 1400-1470°C and a reduction pressure of 103 mbar, the ceria
22	foams produced 281 $\mu$ mol of H $_2$ and 332 $\mu$ mol of CO per gram of material during oxidation below

1000°C under cooling with a maximum production rate of 3.0 mL/min.g and 10.2 mL/min.g,

respectively. Direct syngas production was also evidenced during on-sun experiments with simultaneous H<sub>2</sub>O- and CO<sub>2</sub>-splitting, which yielded a H<sub>2</sub>:CO ratio ranging from 0.7 to 1.14. The dual-

scale porous ceria structures were characterized by XRD, SEM, and TGA to confirm material thermal stability during cycling. Finally, optimization of fuel production capacity was achieved by maximizing the total amount of ceria foam loaded into the reactor, yielding 667 mL of CO (409 µmol/g) and 513 mL of H<sub>2</sub> (314 µmol/g) per cycle. A maximum solar-to-fuel efficiency of 10.1% was calculated for CO<sub>2</sub>splitting versus 4.9% for H<sub>2</sub>O-splitting cycle. This study thus demonstrated noteworthy fuel production performance in an efficient monolithic reactor under real concentrated solar radiation, from highlyreactive customized ceria foams.

Keywords: Hydrogen, Syngas, Water splitting, CO<sub>2</sub> conversion, Thermochemical cycles, Concentrated
 solar energy, Ceria foam.

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### 36 **1. Introduction**

The sustainable production of hydrogen or syngas (H<sub>2</sub>+CO mixture) fuel is a major challenge for today's 37 38 society because it could advantageously replace the consumption of fossil fuels. Innovative solutions 39 must be developed to produce such energy carriers without emitting greenhouse gases or consuming 40 fossil fuel resources. First commercial deployments of sustainable hydrogen fabrication are emerging 41 in 2023 with hydrogen production plants that use renewable electricity from wind energy to produce 42 "green" hydrogen by electrolysis [1]. Other pre-commercial projects focus on hydrogen production 43 from photovoltaic electricity still using electrolysis [2]. Nevertheless, this approach suffers from low overall energy conversion performance due to low power generation efficiency. Alternative solutions 44 45 to electrolysis from renewable energy sources could be more effective and could allow the production 46 of sustainable hydrogen or syngas with lower production costs. From the proposed multiplicity of 47 alternative pathways, multi-step thermochemical processes using concentrated solar energy appear 48 as a credible route to produce hydrogen or syngas [3],[4],[5]. Two-step thermochemical cycles 49 involving metal oxide redox pairs to split  $H_2O$  and/or  $CO_2$  have been investigated for several decades, 50 as reported in numerous review papers [6]-[10]. The thermochemical process involves redox pairs to dissociate  $H_2O$  (or  $CO_2$ ) molecules into separate streams of  $H_2$  (or CO) and  $O_2$ . These cycles are composed of an activation step, consisting of the partial metal oxide reduction (Eq. 1), followed by a hydrolysis step leading to the release of  $H_2$  (or CO) (Eq. 2).

$$M_x O_y \rightarrow M_x O_{y-\delta} + \delta/2 O_2 \tag{1}$$

55 
$$M_xO_{y-\delta} + \delta H_2O (+ \delta CO_2) \rightarrow M_xO_y + \delta H_2 (+ \delta CO)$$
 (2)

54

The first reaction (partial oxide reduction) is endothermal requiring thermal energy provided by concentrated solar radiation. This reaction occurs at a temperature significantly lower than the direct single-step thermolysis of water (T > 2500°C) but still requires temperatures of about 1400°C achievable with concentrated solar energy. The second reaction (oxidation) is exothermic and requires no solar energy input (provided the temperature is high enough for the reaction kinetics). The conversion efficiency is not limited by any intermediate electricity production step and could theoretically exceed the conversion efficiency of electrolysis [5],[11],[12].

63 Currently, the measured performance of such processes is still low ( $\eta_{solar-to-syngas}$  below 5%, defined as the ratio of the higher heating value of the syngas produced to the sum of solar energy input Qsolar and 64 65 any other parasitic energy inputs such as those associated with vacuum pumping and/or inert gas 66 consumption) [13],[14]. Different types of solar thermochemical reactors have been already studied 67 applying ceria as redox material. Some reactors are using moving materials such as the aerosol reactor 68 for the reduction step by indirect heating [15], the moving packed-bed reactor [16], or the rotary-type 69 reactors [17], [18]. Stationary oxides are used in other monolithic reactor concepts such as honeycomb 70 [19], or cavity reactors [20],[21],[22], allowing to proceed both reaction steps in the same reaction 71 chamber. Theoretical investigations on thermodynamics reveal a maximum solar-to-fuel efficiency of 72 12.9% using ceria [23]. The main limitation to improving efficiency comes from the characteristics of 73 the redox material. Indeed, kinetic [24], [25] or thermodynamic [26], [27] limitations of the currently 74 used redox materials (such as CeO<sub>2</sub>, NiFe<sub>2</sub>O<sub>4</sub> or lanthanum-manganite perovskites La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>3</sub>) lead 75 to low reduction capability or limited hydrogen or syngas production output per cycle. These fuel production performances could be increased by using either new materials with improved redox
properties (rapid kinetics, high reducibility) and/or by optimizing the operating conditions.

78 New perovskite formulations or high entropy oxides (HEO) have been studied to find the best-in-class 79 material that will allow a profitable solar thermochemical hydrogen or syngas production. Several 80 review papers have been published on perovskites thermodynamics, design principles and 81 experimental results [28]-[30]. All mention that perovskites can accommodate huge composition 82 space, are thermally stable in the solid phase, and can accept large oxygen non-stoichiometry without 83 phase change. From the broad compositional possibilities, computational calculations and 84 experimental screening studies have identified lanthanum-manganese, lanthanum-cobalt, and 85 yttrium-manganese, together with other dopants, as promising candidate perovskites for solar 86 thermochemical cycles. These perovskites enable a decrease in the reduction temperature to reach a 87 given degree of reduction compared to ceria, but their relatively low reduction enthalpies lead to a 88 lower reactivity for the splitting step. All the reported perovskites need high excess of steam or  $CO_2$  to 89 complete re-oxidation, which negatively impacts the solar-to-fuel efficiency. Regarding high entropy 90 oxides, Zhai et al. reported a high hydrogen production yield of 10.1 mL/g with (FeMgCoNi)Ox[31], and 91 Gao et al. also investigated such a material showing high production yields during microwave-assisted 92 hydrogen production [32],[33]. Within the frame of the American project "HydroGEN: Advanced water 93 splitting materials", new high entropy perovskite oxides (HEPO) have been studied [34]. This 94 potentially transformative new class of water splitting materials is being investigated with a H<sub>2</sub> yield 95 target of 400 µmol/g operating for 50 one-hour cycles (reduction and oxidation). An experimental 96 screening of new HEO compositions for application in solar thermochemical cycles was also published 97 in 2022 [35].

98 In addition to the formulation of materials, the improvement of the involved solid/gas reactions could 99 also be achieved by a relevant material shaping. Indeed, by increasing the volumetric absorption of the 100 concentrated solar radiative flux, or by increasing the porosity and the specific surface area, the overall 101 reactivity could be improved. Reticulated foams have shown attractive results with ceria [36]-[41].

102 Pullar et al. reviewed ceria-based ceramics with designed morphologies and microstructure in 2019 103 [42]Erreur ! Source du renvoi introuvable. and reported an influence of porosity and microstructure 104 on reactivity, although the comparison is not trivial due to heterogeneity of procedure and 105 experimental conditions (partial pressure  $pO_2$ , temperature, time, loaded mass). Ceria fibbers 106 [43],[44], ceria felts [45], reticulated porous ceria [46], ceria microspheres [47] or 3D-ordered 107 microporous ceria [48], [49], have been studied, showing increased amount of produced fuel compared 108 to unshaped ceria powders [50]. Perovskite-coated ceria foams were also found to offer improved  $CO_2$ 109 and H<sub>2</sub>O splitting performance [51].

110 The present study deals with the synthesis and characterisation of custom-made reticulated ceria 111 foams with the aim to improve solar  $H_2/CO$  production. A comprehensive study ranging from material 112 synthesis and microstructure optimization to performance testing in a solar reactor under real 113 environmental conditions (high solar flux and high temperatures) is reported, along with the 114 investigation of the impact of the main operating parameters controlling the process. The methods 115 employed to improve materials and solar thermochemical conversion outcome were studied. A 116 detailed parametric study was carried out to determine the main parameters influencing  $CO_2$  and  $H_2O$ 117 splitting (Section 3.2). The reactive material for redox cycling was prepared as reticulated porous foams 118 with improved morphology and microstructure suitable for solid-gas reactions and solar radiation 119 absorption. Dual-scale porous ceria structures were synthesized by using the replication method with 120 the addition of filamentous porogens. The pristine redox-active foams were characterized and then 121 cycled in a cavity reactor under concentrated solar irradiation. During the on-sun experimental 122 campaign, numerous operational parameters were investigated and optimized to improve H<sub>2</sub>/CO 123 production. Cyclability tests were carried out over several consecutive cycles for splitting  $CO_2$  and  $H_2O$ 124 to show performance stability. Process/reactor optimization was a key aspect of the work as the 125 objective was to optimize the fuel productivity and efficiency. Performance/efficiency were evaluated 126 under various operating conditions, closely representative of a real solar process. Results showed that 127 the fuel production rate is greatly affected by various parameters including pressure during reduction,

temperature during oxidation, oxidant mole fraction or oxidant gas flow-rate (Sections 3.2.1 and 3.2.2). Operational strategies can thus be optimized by focusing on tuning these parameters. Processing limitations regarding the simultaneous co-feeding of H<sub>2</sub>O and CO<sub>2</sub> for direct syngas production were also unravelled (Section 3.2.3). The amount of loaded material in the reactor was finally optimized for maximum fuel production capacity (Section 3.3). Results were compared to the best-in-class materials in order to confirm that solar fuel production performance can be improved by a relevant material shaping, while optimizing its total loaded amount and cycling conditions.

- 135 **2. Experimental methods**
- 136 2.1. Materials synthesis

Reticulated ceramic foams were synthesized using the replication method described elsewhere [52].
An aqueous slurry was first realized with the defined oxide powder, the porogen, and organic additives
(see Table 1).

140 Table 1. Components in the slurry used to make foams via the replication method (the percentages

141

are expressed in relation to the mass and volume of ceria).

Slurry components	Name/composition/provider	Proportion
Paw material	Ceria	~
Raw material	(Sigma-Aldrich, 99.9%, <5 μm powder)	111
Solvent	Water	m/3
	Carbon fibbers	
Porogen	(Sigrafil <sup>®</sup> M80-3.0, filaments	30 vol%
	7 μm diameter and 80 μm long)	
Pindor	Polyvinyl alcohol	1 2E wt%
billuei	(Mowiol)	1.55 WL/6
Disporsant	Dolapix	0 9E wt%
Dispersaill	(Zschimmer & Schwarz GmbH)	0.03 WL%

Then, a sacrificial polyurethane template (interconnected open-cell foam with a pore density of 10 ppi) was plunged once into the slurry and dried overnight at room temperature. The as-impregnated foam was then slowly heated up to 1000°C (at 2.5°C/min) to remove the organic components of the foam precursor, and annealed at 1400°C during 3 hours to achieve sintering that provides a mechanical strength to the foam. Polyurethane discs and rings with a diameter of 54 mm and a thickness of 20 147 mm were coated with the slurry described above. Figure 1.a shows the grey colour of the disc before 148 calcination due to the carbon fibbers porogen. After calcination at 1400°C, the foam contains only CeO<sub>2</sub> 149 and becomes yellowish (Fig. 1.b). The sintering phenomenon causes a shrinkage of the foam of  $15\%_{vol}$ . 150 The foams have a final diameter of 46 mm, slightly less than the diameter of the cavity in the solar 151 reactor, therefore suitable for their loading inside the cavity. Optical microscopy was used to 152 characterize the morphology of the foams. The polyurethane template was completely eliminated and 153 left empty spaces inside strands (Fig. 1.c. and 1.d). The optical shadow effect mode permits to observe 154 the porous surface of the foam (Fig. 1.e). Higher magnifications obtained with SEM allow an 155 observation of well-distributed interconnected cylindrical pores of about 80 µm in length and 8 µm in 156 diameter (see Section 3.4). This high porosity, obtained thanks to the porogenic carbon fibbers, should 157 promote the diffusion of gas species inside the struts and thus improve the reactivity in the bulk. The 158 dual scale porosity allows both good penetration of the solar radiative flux and diffusion of gases inside 159 the material. The mass of such ceria foams depends on the thickness of the coating during 160 impregnation. Reticulated ceria discs 46 mm in diameter and 17 mm in height weight approximately 161 30 g. This corresponds to a bulk density of 1.06 g/cm<sup>3</sup>. By comparison with the density of ceria ( $\rho = 7.13$ g/cm<sup>3</sup> – data from Sigma-Aldrich), a porosity of 85% is calculated. 162



- Figure 1. Images of porous CeO<sub>2</sub> foams obtained by the replication method: (a) photograph of the
  polyurethane foam coated with the slurry before calcination, and (b) after calcination. (c), (d), (e)
  Optical microscopy of a CeO<sub>2</sub> foam after calcination. (f) Image in shadow effect mode of a foam
  strand.

174 2.2 Characterization

175 The structure and microstructure of the prepared ceria foams were fully characterized with the 176 following series of techniques.

177 The crystalline structure was studied by X-ray diffraction (XRD) using a Panalytical X'PERT PRO 178 diffractometer with the Cu K $\alpha$  radiation ( $\alpha$ Cu = 0.15406 nm, angular range = 20-80°, 2 $\theta$ , tube current 179 20 mA, potential 40 kV).

180 The morphology of the foams was first observed with a Keyence VHX digital microscope equipped with 181 a VHXAnalyser software. In addition, a Field Emission Scanning Electron Microscope (FESEM - Hitachi S4800) was used to observe the microstructure of ceria foams before and after thermochemical cycles. 182 183 Thermogravimetric analysis (TGA, SETARAM Setsys Evo 1750) was used to measure the mass variations 184 (amount of oxygen exchanged) associated to the reduction and the oxidation steps of thermochemical 185 cycles. The sample was heated under argon flow (20 mL/min) with a heating rate of 20°C/min up to 186 the selected set-point temperature, and the mass variation was recorded continuously. The successive 187 steps of cycles were carried out at different temperatures (typically 1400°C dwelled for 45 min during 188 the reduction step and 1050°C dwelled for one hour during the CO<sub>2</sub>-splitting step) and CO<sub>2</sub> was injected

during the oxidation step (50%  $CO_2$  in Ar with a  $CO_2$  flowrate of 10 mL/min).

190 2.3 Solar reactor

191 Figure 2 shows a scheme of the solar reactor developed in our previous work [36]. It consists of a 192 cylindrical water-cooled stainless-steel vessel in which an insulated alumina cavity is placed. The 193 reactor is capped with a hemispherical window of transparent Pyrex glass that allows concentrated 194 solar flux to enter the cavity, and that separates the reactive materials and reaction chamber from the 195 outside atmosphere. Three B-type thermocouples are positioned along the height of the cavity in 196 contact with the foam to measure the temperature. A solar-blind pyrometer, placed vertically to the 197 cavity, is used to measure the temperature of the foam in a central point (in the foam cavity at the 198 center of the rings). The T1 thermocouple, which is used as temperature reference, is placed in contact 199 with the external side of a foam at 20 mm from the bottom of the cavity, whereas the pyrometer 200 measures the temperature in the middle of the foam cavity formed by the rings. Several pressure 201 sensors are fitted to the reactor to monitor the pressure inside the cavity and at the gas inlets. The 202 reticulated foams are positioned in the cavity. The sweep gas (Ar, 99.999% purity,  $p_{02} = 10^{-5}$  bar) can 203 flow from the top of the cavity and/or from the side, and the gas outlet is located under the reactive 204 materials at the cavity bottom. Therefore, the gas flows through the reticulated foams. CO<sub>2</sub> (99.995% 205 purity) and/or steam are injected from the side of the cavity. To produce steam, liquid water is injected 206 through a liquid mass flow controller (range 0-60 g/h) in an alumina capillary connected to the cavity. 207 The liquid water is vaporized before entering the cavity and transported by the inert sweep gas. The 208 gas outlet is connected to an O<sub>2</sub> trace analyser (electrochemical cell) and an H<sub>2</sub> analyser (catharometer) 209 or CO analyser (NDIR sensor) to measure gas concentrations on-line. When co-feeding H<sub>2</sub>O and CO<sub>2</sub>, a 210 syngas analyser (Emerson XStream) is used to monitor the gas species concentrations continuously 211 and simultaneously (especially  $H_2$  and CO). For the experimental campaign, the reactor is placed at the 212 focus of a vertical-axis solar furnace. A solar concentrator (2 m diameter parabolic dish) of 1.5 kW 213 (thermal) is used to concentrate the solar radiation coming from a sun-tracking heliostat located 30 m 214 below the reactor frame (the reactor thus does not need to be moved as only the heliostat two-axis 215 tracking is used to follow the sun's position). The process heat source is therefore real concentrated 216 solar energy provided by the solar furnace. A shutter is placed between the heliostat and the parabola 217 to control the solar power input during thermochemical cycles. A calibration curve is used to calculate 218 the solar power input as a function of the shutter closing and the DNI (Direct Normal Irradiation). A 219 vacuum pump is used to purge the reactor prior to experiments to remove oxygen and to control the 220 total pressure in the cavity during the cycle reduction step.



Figure 2. Scheme of the solar reactor.

223 The experimental protocol is described in the following. Ceria foams are first weighted and placed in 224 the cavity. A full disc is placed at the bottom and two rings are positioned above the disc. The reactor 225 is purged with argon until the oxygen outlet concentration is below 10 ppm. The inert gas flow is 226 regulated at the desired value with a mass flow meter. The total pressure in the reactor is set by using 227 a vacuum pump (po2 depends directly on the reactor total pressure). Then, the ceria foams are 228 gradually heated by opening the shutter of the concentrator until reaching the desired temperature 229  $(T1 = 1400^{\circ}C)$ . This stage corresponds to the reduction step of the cycle and oxygen is continuously 230 released by ceria during heating. Once the temperature is reached, a plateau is maintained. The oxygen 231 concentration decreases until thermodynamic equilibrium of ceria foam reduction is reached (~ 45 232 min), indicating that the reduction step is completed. In this work, we did not seek to minimize the 233 duration of the reduction step and therefore we rather used sufficiently long durations (slow heating 234 rates with long enough temperature dwells during reduction) to ensure that the O<sub>2</sub> concentration 235 returns to negligible values (thereby ensuring a reduction step close to equilibrium) before proceeding 236 to the oxidation step. Moreover, during reactor heating the solar power input P<sub>solar</sub> was not at its 237 nominal value but was gradually increased by opening the shutter to progressively heat the system. 238 The total oxygen release per gram of ceria is calculated by integrating the  $O_2$  concentration in the 239 exhaust gas over the reduction time. It is important to note that the oxygen partial pressure  $(p_{02})$ 240 during the reduction step is not constant in the reactor and varies greatly between the inlet (inert gas), 241 the ceria foam, and the outlet of the reactor. It further depends on the time-dependent rate of  $O_2$ 242 production from the material (hence on the temperature and heating rate). For the oxidation step, the 243 shutter is then closed to decrease the temperature. The re-oxidation step is carried out under non-244 isothermal conditions, which means that steam or  $CO_2$  is injected during free cooling (without solar 245 heating) from a defined temperature, but there is no dwell and the temperature drops continuously 246 during this step (about 5 min). The argon and steam/CO<sub>2</sub> flows are regulated to the desired values by 247 using mass flow meters. H<sub>2</sub>/CO concentrations in the exhaust gas are recorded on-line and integrated 248 over time to calculate the total H<sub>2</sub>/CO production per gram of ceria. Figure 3 shows a schematic 249 representation of the ceria foams in the cavity and different pictures of the solar reactor during the 250 experimental campaign.



258 XRD patterns of the crushed foams before and after cycling are presented in Figure 4. The ceria phase

is observed and compared to pure ceria powder. The diffraction peaks are sharpened indicating an

increase of the crystallite size caused by the thermal treatment. Crystallite size calculation using the Scherrer formula gives a size of 79 nm for the powder and 106 nm for the foam before and after thermochemical cycling. The size of the crystallites thus remains almost unchanged during the thermochemical cycles. This means that the crystalline domains were stabilized before cycling experiments, thanks to the high temperature of the heat treatment in air during the preparation of the foam, and crystallite sizes did not evolve significantly during cycles.



267

266

Figure 4. XRD patterns of ceria foams before and after cycling

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(pure ceria powder is reported for comparison).

269 Thermogravimetric analysis of both the commercial ceria powder and the derived custom-made ceria 270 foam were carried out (Fig. 5). Two consecutive CO<sub>2</sub>-splitting cycles were realized with a reduction 271 temperature of 1400°C and an oxidation temperature of 1050°C. During the reduction steps at 1400°C, 272 the ceria powder released 55 and 54  $\mu$ mol/g of O<sub>2</sub> and the ceria foam released 47 and 51  $\mu$ mol/g of O<sub>2</sub>. The CO production yields were 94 and 98 µmol/g with the ceria powder, and 99 and 96 µmol/g 273 274 with the ceria foam. No significant change was observed between the two cycles, except the kinetic of 275 re-oxidation during the first cycle. The ceria foam presents a steep mass increase that is explained by 276 the dual porosity of the foam that improves the kinetics of CO<sub>2</sub> splitting.



278 Figure 5. TGA of the commercial ceria powder and derived custom-made foam during two consecutive

277

## *CO*<sub>2</sub>-splitting cycles.

A campaign of experimental solar tests was then carried out with the custom-made ceria foams shaped to fit the cavity of the solar reactor. A disc of 46 mm diameter and 17 mm high, and two rings of the same diameter and height were inserted into the solar reactor cavity (Figure 3). It represents a load of approximately 50 grams of active material.

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# 285 3.2 Parametric study with the $CeO_2$ foams in the solar reactor

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A parametric study was carried out with the aim of optimizing the production performance of solar fuel (H<sub>2</sub>/CO). Consecutive cycles of CO<sub>2</sub> and H<sub>2</sub>O dissociation were performed to study the effect of various operating conditions on fuel production rates and yields. The reduction temperature was set at 1400°C (T1) and the parametric study focused on various parameters including the pressure of the reduction step (P<sub>red</sub>), the temperature of the oxidation step (T<sub>ox</sub>), the total gas flowrate during oxidation (Q<sub>ox</sub>), and the reactive gas concentration (CO<sub>2</sub>/H<sub>2</sub>O).

293

3.2.1 CO<sub>2</sub> dissociation cycles

294 Two series of  $CO_2$ -splitting cycling experiments were performed with the same foams (total loaded 295 mass m = 50.02 g). Five consecutive cycles were realized during the first series and three consecutive 296 cycles during the second one. Figure 6 presents the temperature profile of the foam near the bottom 297 of the cavity (T1 in Fig. 2), the temperature measured by the pyrometer, and the evolution of gas 298 species production rates (O<sub>2</sub> and CO). Note that gas rates are scaled with two different axes, otherwise 299 the  $O_2$  production rate profile would not be visible as its outlet concentration is much lower than the 300 CO concentration (CO exhibits fast production rate whereas O<sub>2</sub> production profile is much longer). The 301 values of peak production rates are reported in Table 2. The influence of several experimental 302 parameters was investigated such as the total pressure during reduction, the oxidation temperature, 303 and the CO<sub>2</sub> flowrate. For all experiments, the reduction temperature was set at 1400°C (T1) and argon 304 was injected both in the window area ( $Q_{Ar,top}=1$  NL/min) and at the top of the cavity from the side 305 (Q<sub>Ar,cavity</sub>=0.2 NL/min). The temperature measured by the pyrometer was ~70-100°C higher during 306 heating and dwells, thus revealing a temperature gradient inside foams along the height. The average 307 temperature of the foam was thus above 1400°C and was between the temperature of the pyrometer 308 and T1. Reaching a perfectly homogeneous temperature through the foam heated by concentrated 309 solar radiation is not possible, unlike conventional heating devices such as perfectly-controlled electric 310 ovens. Since the ceria reduction process is highly sensitive to temperature, which greatly affects the 311 extent of oxygen non-stoichiometry  $\delta$ , it should be noted that the specified reduction temperature of 312 1400°C was the control temperature at T1 but the top of the foam was above this temperature.

Table 2 reports the results of CO<sub>2</sub> splitting cycles for each experimental condition. During the three first cycles, the O<sub>2</sub> production yield reached 97, 100, and 99 µmol/g ( $\delta \sim 0.034$ ) for a total pressure of 870 mbar (atmospheric pressure in Odeillo laboratory in Pyrenees mountains) during the reduction step. This reduction yield was well reproducible during cycles #1, #2, and #3, all carried out under the same experimental conditions (Q<sub>Ar</sub>=1.2 NL/min, T<sub>red</sub>=1400°C). Since the controlled temperature (T1) was located near the foam bottom, the upper part of the material was actually above this temperature (as denoted by the pyrometer measurement). Due to this temperature gradient, the global reduction yield was higher than the one measured in TGA. The associated CO production yield, with CO<sub>2</sub> injection starting at 1000°C during cooling, was 245, 229, 226 µmol/g for cycle #1, #2, #3 with peak production rates of 3.3, 2.3, and 3.5 mL/min.g, respectively. The lower peak production rate during cycle #2 is due to a lower cooling rate during the oxidation step, as observed in Figure 6. These production rates and yields are consistent with previously reported values for ceria foams [36].

By decreasing the total pressure during the reduction step at 292 mbar (cycle #5) and 103 mbar (cycle #4), the oxygen partial pressure was decreased and the O<sub>2</sub> yield was significantly improved up to 123  $\mu$ mol/g ( $\delta \sim 0.042$ ) and 151  $\mu$ mol/g ( $\delta \sim 0.052$ ) respectively, while the associated CO production yields reached 271  $\mu$ mol/g and 321  $\mu$ mol/g, respectively. The CO peak production rate was also improved (3.9 mL/min.g and 4.7 mL/min.g, respectively) when the reduction yield was increased (Figure 7).

330 During cycles #6 to #8, pure CO<sub>2</sub> (mole fraction = 1) was injected at a different flowrate of 2 NL/min 331 (instead of 1 NL/min). The CO production yield reached 332 µmol/g in cycle #6, 318 µmol/g in cycle #7, 332 and 315  $\mu$ mol/g in cycle #8 after a reduction step at 100 mbar (with  $\delta \sim 0.052$ -0.056). This confirms 333 the repeatability and stability of the reactor performance. The CO production yield did not depend on 334 the CO<sub>2</sub> flowrate (comparison between cycles #4 at 1 NL/min and #7 at 2 NL/min), but the peak 335 production rate was improved by injecting higher CO<sub>2</sub> flowrates (8.2 mL/min.g for cycle #7 instead of 336 4.7 mL/min.g for cycle #4). The maximum CO production rates were 8.5 mL/min.g for a CO<sub>2</sub> injection 337 temperature of 1000°C (cycles #6) and 10.2 mL/min.g for an injection temperature of 900°C (cycle #8).







Figure 6. Temperature profiles and gas production rate evolution during  $CO_2$ -splitting solar cycles with CeO<sub>2</sub> foams: (a) cycles #1-5: influence of  $P_{red}$  ( $T_{ox}$ <1000°C and  $CO_2$  flowrate = 1 NL/min), (b) cycles #6-8: influence of  $T_{ox}$  ( $P_{red}$ =100 mbar and  $CO_2$  flow rate = 2 NL/min).

Table 2. Experimental conditions and results of  $CO_2$ -splitting solar cycles with  $CeO_2$  foams (m = 50.02

g).

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Cycle #	Reduction pressure (mbar)	CO2 flowrate (NL/min)	Oxidation temperature start (°C)	O2 yield (µmol/g <sub>ceria</sub> )	CO yield (µmol/g <sub>ceria</sub> )	CO peak production rate (mL/min.g)	CO/O <sub>2</sub> ratio
Cycle 1	874	1	1000	96.9	244.7	3.3	2.5
Cycle 2	879	1	1000	100.2	228.5	2.3	2.3
Cycle 3	879	1	1000	98.6	226.1	3.5	2.3
Cycle 4	103	1	1000	150.6	320.5	4.7	2.1
Cycle 5	292	1	1000	123.3	270.9	3.9	2.2
Cycle 6	100	2	1000	161.8	332.3	8.5	2.1
Cycle 7	100	2	1000	151.9	318.4	8.2	2.1
Cycle 8	100	2	900	155.5	314.7	10.2	2.0

347

This experimental study demonstrates the relevant cyclability of ceria foams, thus offering good repeatability of CO production. Favourable conditions for increasing CO production are a decrease in total pressure during the reduction step (decrease of p<sub>02</sub>), an increase in CO<sub>2</sub> flowrate and a decrease of re-oxidation temperature. Such conditions enhance CO production but can have a negative impact on energy efficiency as (i) higher gas flowrates result in higher energy consumption for heating, (ii) a reduction step at low pressure implies pumping work, and (iii) lowering the temperature during the oxidation step results in sensible heat losses when considering the full cycle.







357

### 3.2.2 Water dissociation cycles

Two series of H<sub>2</sub>O-splitting solar cycling experiments were also realized with the same foams (total loaded mass m = 50.02 g). Several experimental parameters were investigated such as the total pressure during reduction, the total Ar carrier gas flowrate during hydrolysis, and the steam content. Table 3 presents the selected experimental conditions for the reduction and oxidation steps, as well as the results of O<sub>2</sub> and H<sub>2</sub> production. Figure 8 shows the temperature profiles and gas production rates during the 8 thermochemical cycles.

365	Table 3. Experimental conditions and results of H <sub>2</sub> O-splitting solar cycles with CeO <sub>2</sub> foa	ms (m = 50.02 g).
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Cycle #	Reduction pressure (mbar)	Argon flowrate (hydrolysis- NL/min)	H <sub>2</sub> O mole fraction	O₂ yield (µmol/g <sub>ceria</sub> )	H2 yield (µmol/g <sub>ceria</sub> )	H₂ peak production rate (mL/min.g)	H <sub>2</sub> /O <sub>2</sub> ratio
Cycle 1'	868	1.0	29.4%	101.2	203.6	1.5	2.01
Cycle 2'	904	1.0	38.4%	105.4	202.9	1.9	1.93
Cycle 3'	899	1.0	45.4%	105.1	199.0	2.2	1.89
Cycle 4'	103	1.0	45.4%	148.5	280.6	3.0	1.89
Cycle 5'	904	1.0	51.0%	99.8	187.0	2.2	1.87
Cycle 6'	905	1.0	55.5%	97.6	176.9	2.5	1.81
Cycle 7'	902	1.5	35.7%	98.4	182.3	2.2	1.85
Cycle 8'	905	2.0	29.4%	97.3	188.0	2.4	1.93





374 The highest H<sub>2</sub> production yield was 280.6 µmol/g<sub>ceria</sub> during cycle #4' with a low-pressure reduction 375 step (103 mbar), a hydrolysis step at  $T_{ox}$ <1000°C, and a steam content in the sweep gas of 45.4%. The 376 highest H<sub>2</sub> production rate was 3.0 mL/min.g<sub>ceria</sub> that was obtained during the same cycle. This peak 377 rate is lower than in the case of CO<sub>2</sub> because pure CO<sub>2</sub> was used, whereas Ar was used as carrier gas 378 during H<sub>2</sub>O injection, which lowered the steam content in the oxidation step. The optimal parameters 379 to improve the  $H_2$  production are a low-pressure reduction step, a high steam content, and a high gas 380 flowrate during the hydrolysis step. The rate of the hydrolysis step is directly related to the steam 381 content.

382 Figure 9 illustrates the influence of the steam content in the sweep gas during hydrolysis at the same 383 temperature ( $T_{ox}$ <1000°C) and Ar flowrate (1 NL/min). The higher the steam content, the higher the H<sub>2</sub> 384 peak production rate. The steam content only impacts the hydrolysis rate while overall O<sub>2</sub> and H<sub>2</sub> yields 385 remain unchanged. This is because the oxidation step is complete regardless of the steam content. 386 Increasing the Ar flowrate during hydrolysis (cycles #6',7',8') decreases the H<sub>2</sub>O mole fraction but this 387 effect does not impact H<sub>2</sub> production rates and yields. Indeed, the increase in the total gas flow rate 388 promotes the mass transfer of gas species, decreases the molar fraction of H<sub>2</sub> (thereby shifting the 389 reaction equilibrium towards H<sub>2</sub>), and further sweeps the H<sub>2</sub> produced away from the reaction sites, 390 which in turn promotes the hydrolysis reaction.





Figure 9. (a)  $H_2$  production rate evolution and (b) peak production rate as a function of steam content in the sweep gas (cycles #1', 2', 3', 5', 6': reduction step at T1 = 1400°C and other hydrolysis parameters unchanged).

Figure 10 compares the production yields of CO and H<sub>2</sub> by solar thermochemical cycles with ceria foams
over the entire solar experimental series. The cycling capability is highlighted as no deactivation was
observed regarding O<sub>2</sub> release during the reduction steps. About 100 µmol/g of O<sub>2</sub> was released during
reduction steps at T1 = 1400°C under a total pressure of ~900 mbar. The dissocation of CO<sub>2</sub> appears to
be more efficient than H<sub>2</sub>O splitting, which is mainly the result of the different concentration of oxidant
gas during the oxidation step. Indeed, a pure CO<sub>2</sub> stream was used while no experiment could be
conducted with pure steam injection due to technical constraints.



404 Figure 10. Comparison of O<sub>2</sub> and CO/H<sub>2</sub> production yields during 16 consecutive solar thermochemical
 405 cycles using ceria foams and different experimental conditions.

403

407 3.2.3 Simultaneous H<sub>2</sub>O and CO<sub>2</sub> dissociation cycles for syngas production

408 In order to complete the on-sun experimental campaign with ceria foams, simultaneous CO<sub>2</sub>- and H<sub>2</sub>O-409 splitting cycles were performed to produce syngas. The reduction steps were carried out under low 410 pressure (115 mbar) with a flow of Ar (1.2 NL/min), and the oxidation steps were carried out at 411  $T_{ox}$ <1000°C with 41% steam (50 g/h), 39% CO<sub>2</sub> (1 NL/min), and 20% Ar (0.5 NL/min) as sweep gas 412 composition (Table 4). Steam and CO<sub>2</sub> flowrates were chosen to have a similar concentration in the 413 flowing gas and to not favour one reaction over another when simultaneous splitting. Three consecutive splitting cycles were performed and Figure 11 shows the temperature profiles and gas 414 415 production rates. The maximum production rate of CO was higher than  $H_2$  with respectively 4.6, 3.8, 416 and 3.2 mL/min.g and 1.7, 1.4, 2.2 mL/min.g (Table 4).





421 Figure 11. Temperature profiles and gas production rate evolution during simultaneous CO<sub>2</sub>- and H<sub>2</sub>Osplitting solar cycles with  $CeO_2$  foams: (top) overall successive cycles, (bottom) zoom on CO and  $H_2$ 422 production peaks (cycles #1"-3").

424

425 Figure 12 shows the cumulative production yields of O<sub>2</sub> during the reduction steps and of CO and H<sub>2</sub> 426 during the reoxidation steps. The O<sub>2</sub> amounts released during low pressure (115 mbar) reduction steps 427 at T1 = 1400°C reached 137, 137, and 145 µmol/g for the three consecutive cycles (Table 4). During the 428 first and second cycles, the CO production yield was higher than the H<sub>2</sub> production yield (144.6 and 160.7 µmol/g for CO against 114.7 and 111.9 µmol/g for H<sub>2</sub>). In contrast, during the third cycle, the 429 430 production of H<sub>2</sub> was higher than the production of CO (159.0 and 138.5  $\mu$ mol/g, respectively). This 431 trend could be explained by the difference in reactive gas injection time. Indeed, the first gas species 432 entering the cavity react first preferably with the surface sites of the ceria foams, and it is 433 experimentally difficult to control which one will enter the reactor first. A very short delay in oxidant 434 gases injection (small lag between H<sub>2</sub>O and CO<sub>2</sub> injections) results in a significantly different syngas 435 composition. Operating perfectly simultaneous gases injection is challenging and may represent a 436 process limitation when co-feeding  $H_2O$  and  $CO_2$  for  $H_2$ :CO ratio control. Direct syngas production by co-feeding of H<sub>2</sub>O and CO<sub>2</sub> did not turn to be advantageous for precise control of the syngas 437 438 composition. Nevertheless, the sum of CO and H<sub>2</sub> production yields lead to full reoxidation extent with 439 a (CO+ $H_2/O_2$ ) ratio equal to 1.9 or 2.

440



441



Figure 12. Cumulative gas production evolution (O<sub>2</sub> and syngas) and temperature profile for three 443 consecutive thermochemical cycles operated on-sun with  $CeO_2$  porous foams

Cycle #	O2 (µmol/ g <sub>ceria</sub> )	CO yield (µmol/g <sub>ceria</sub> )	CO maximum production rate (mL/g.min)	H2 yield (µmol/ g <sub>ceria</sub> )	H <sub>2</sub> maximum production rate (mL/g.min)	CO + H <sub>2</sub> (µmol/g <sub>ceria</sub> )	(CO+H <sub>2</sub> )/O <sub>2</sub>
Cycle 1"	136.9	144.6	4.6	114.7	1.7	259.3	1.9
Cycle 2"	137.4	160.7	3.8	111.9	1.4	272.6	2.0
Cycle 3"	145.3	138.5	3.2	159.0	2.2	297.5	2.0

447

### 448 3.3 Effect of total loaded mass of ceria foams

449 The amount of fuel produced per cycle can be further improved by increasing the total amount of 450 reactive ceria loaded in the reactor cavity. Redox cycles were carried out with a higher charge of ceria 451 foams (72.9 g) in the solar reactor to optimize fuel yield and analyse the energy balance. This was 452 achieved by preparing ceria foams with higher bulk density and increasing the number of stacked rings 453 to fully fill the volume of the reactor cavity (a bottom disc and three rings were used in this case). The 454 goal was to utilize the reactor's maximum loading potential to optimize the reactor's fuel production 455 capacity. Two consecutive CO<sub>2</sub> splitting cycles were carried out with a reduction step at low-pressure 456 (105 mbar) and an oxidation step at  $T_{ox}$ <1000°C with 66% CO<sub>2</sub> gas flowing into the cavity (2 NL/min CO<sub>2</sub> 457 and 1 NL/min Ar). In addition, two  $H_2O$  splitting cycles were carried out with low-pressure during 458 reduction first (105 mbar) and atmospheric pressure (900 mbar). The oxidation steps were operated at  $T_{ox}$ <1000°C and  $T_{ox}$ <900°C with 60 g/h H<sub>2</sub>O and 1 NL/min Ar. 459





463 Figure 13. Temperature profiles and gas production rate evolution during (a) CO<sub>2</sub>-splitting and (b) 464  $H_2O$ -splitting solar cycles with maximized loading of  $CeO_2$  foams (m = 72.9 g) in the solar reactor.

Table 5 presents the O<sub>2</sub> and CO/H<sub>2</sub> yields produced during these cycles. The quantities of O<sub>2</sub> produced 465 466 during the reduction steps were higher than the previous values measured under the same conditions 467 (212.5, 198.9, and 198.1  $\mu mol/g$  at 105 mbar and 116.0  $\mu mol/g$  at 900 mbar). The  $\delta$  values were thus 468 also higher (maximum  $\delta \sim 0.073$  in cycle #1<sup>'''</sup>). This is explained by the larger amount of ceria placed

469 in the cavity and the different total height. Indeed, a disc and three rings of ceria foams were inserted 470 in the cavity and the first ring was located at the top of the cavity directly heated by concentrated solar 471 radiation. Therefore, the topmost ring was heated to a higher temperature even though the 472 temperature profile of T1 and the pyrometer did not show such temperature increase at the top of the 473 cavity compared to previous experiments. CO production reached 408.5 and 404.0  $\mu$ mol/g during the 474 oxidation steps (representing 9.1 and 9.0 mL/g) and the H<sub>2</sub> production yields reached 314.3 and 204.8 475 µmol/g. These amounts of CO and H<sub>2</sub> overpass the previous values measured under the same 476 conditions, which were respectively 332.3 µmol/g (cycle #6 in Table 2) and 280.6 µmol/g (cycle #4' in 477 Table 3 at low pressure and  $T_{ox}$ <1000°C). The CO:O<sub>2</sub> ratio was 1.9 and 2.0, which confirms a total re-478 oxidation of the reduced ceria by CO<sub>2</sub>, whereas the H<sub>2</sub>:O<sub>2</sub> ratio was 1.6 and 1.8, which denotes a partial 479 re-oxidation of reduced ceria with water. This can be explained by the steam injection inlet which is 480 placed on the side of the cavity at a height lower than the topmost ceria ring. Therefore, the steam 481 was not distributed over the top of the cavity because the sweep gas (Ar) flows from the top and carries 482 the steam down. This phenomenon was not observed with CO<sub>2</sub> because it was injected both from the 483 top and from the side of the cavity. The total amounts of CO produced during the two cycles were 667 484 mL and 659 mL, respectively, while the total amounts of H<sub>2</sub> produced per cycle were 458 mL and 334 485 mL. Optimization of the fuel production capacity was thus successfully achieved by maximizing the 486 total amount of ceria foam loaded into the reactor.

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Table 5. Results of CO<sub>2</sub>- and H<sub>2</sub>O-splitting cycles with 72.9 g of ceria foams in the solar reactor.

Cycle #	Reductio n pressure (mbar)	CO <sub>2</sub> or H <sub>2</sub> O mole fraction	O2 (µmol/gc <sub>eria</sub> )	CO (µmol/g <sub>c</sub> <sub>eria</sub> )	CO maximum productio n rate (mL/g.min )	H2 (µmol/gc <sub>eria</sub> )	H <sub>2</sub> maximu m producti on rate (mL/g.mi n)	(CO or H2)/O2
Cycle 1‴	105	66%	212.5	408.5	7.1	-	-	1.9
Cycle 2"	105	66%	198.9	404.0	6.9	-	-	2.0
Cycle 3"	105	55.5%	198.1	-	-	314.3	3.2	1.6
Cycle 4"'	900	55.5%	116.0	-	-	204.8	3.4	1.8

	(T <sub>ox</sub> < 900°C)
489	

490 Figure 14 presents SEM pictures of a ceria foam before and after thermochemical cycling under 491 concentrated solar radiations. It is observed that the thickness of ceria strands does not change after 492 thermal cycling (Fig. 14 right). Cylindrical pores of 8 µm diameter and 80 µm long are observed in both 493 cases. Nevertheless, the material seems to slightly densify after thermochemical cycling. The ceria 494 grain size is also increased after thermal cycling (unlike the crystallite size that remains unchanged 495 according to XRD, Fig. 4). The grains grow from 5 µm to 20 µm. A grain can be composed of several 496 crystallites (crystalline domains). Grain growth is observed by SEM due to agglomeration of crystallites. 497 These observations confirm the good thermal stability of the developed porous ceria foams under 498 concentrated solar energy and demonstrate that grain growth has no influence on CO2 and H2O 499 splitting rates and yields.



500



Figure 14. SEM pictures of a ceria foam before (left) and after (right) the whole series of solar CO<sub>2</sub> and
 H<sub>2</sub>O thermochemical cycles at 1400°C.

505 The solar-to-fuel efficiency during the peak production (real-time efficiency) can be calculated by the 506 following equation [16]:

502

$$\eta_{solar-to-fuel} = F_{fuel}.HHV_{fuel}/P_{solar}$$

(3)

where  $F_{fuel}$  denotes the CO or H<sub>2</sub> production rate (mol/s), HHV<sub>fuel</sub> the higher heating value of CO (= 283 kJ/mol) or H<sub>2</sub> (= 286 kJ/mol), and P<sub>solar</sub> the maximum solar power input during the reduction step (kW). Such real-time efficiency eliminates the influence of arbitrary process conditions such as the duration of the reduction step or the effect of weather conditions. Auxiliary power inputs are not taken into account such as pumping works, inert gas regeneration, solar tracking, etc.

513 Psolar only relates to the reduction step because no heating was applied during the oxidation step (free 514 cooling). Table 6 reports the results of the solar-to-fuel efficiency calculations with 72.9 g of ceria 515 foams. CO<sub>2</sub>-splitting cycles are more efficient compared to H<sub>2</sub>O-splitting cycles with peak solar-to-fuel 516 efficiencies of 10.1% and 9.8% for CO<sub>2</sub> splitting against 4.5% and 4.9% for H<sub>2</sub>O splitting. These values 517 are higher than the previously reported ones. For example, Haeussler et al [36] reported a solar-to-518 fuel efficiency of 7.5% for CO<sub>2</sub> splitting in the same reactor (P<sub>red</sub>=110 mbar, T<sub>Ox</sub>=900°C, Q<sub>CO2</sub>=2 NL/min), 519 but with different ceria foams. When considering the total solar energy input integrated over the 520 reduction step duration, an average energy efficiency can be estimated. However, such an efficiency is strongly dependent (inversely proportional) on the duration of the reduction step which can be 521

522 artificially lowered by using high heating rates, in turn drastically increasing the efficiency. This 523 duration is thus arbitrary and depends on the applied experimental protocol. This is typically the case 524 in reactors using an electrical heating source (Xe-lamp based simulators) with facile control of heating 525 rate, which thus artificially boosts the efficiency. Accordingly, the reduction step duration was 526 commonly kept extremely short [21] and consisted in heating the material very fast up to 1500°C and 527 stopping immediately the heating (thus not applying any temperature dwell at the maximum 528 temperature) although the oxygen release equilibrium was not reached. As a result, the whole 529 duration was less than 10 min in [21] thus minimizing the amount of energy consumed and yielding 530 5.25% efficiency, compared with ~50-70 min (with varying solar power input) in the present study 531 yielding ~0.3-0.5% efficiency. In summary, when aiming to reduce the amount of solar energy 532 consumed while increasing the efficiency, the reduction step duration can be shortened by (i) using 533 fast heating up to higher temperatures (e.g., 1500°C) to enhance the reduction extent, and (ii) stopping 534 the solar power input before waiting for complete equilibrium without significantly affecting the 535 amount of oxygen produced. However, beyond the efficiency the most important metrics of the 536 material and process performance are rather the fuel production rates and global fuel yields per unit 537 mass of reactive material. This study showed that improving solar fuel production performance was 538 possible by suitable tuning of material structure and process conditions.

539 In summary, the main novel outputs raised by the study are the followings:

A reactive material for redox cycling was prepared as reticulated porous foams with improved
 morphology and microstructure suitable for solid-gas reactions and solar radiation absorption. In
 particular, foams with dual-scale porosity were obtained by using the replication method thanks to the
 addition of filamentous pore formers in the slurry.

The reticulated foams were cycled in a solar reactor to determine the fuel production performance
 under realistic conditions, with continuous online monitoring of the evolved gas species produced
 during reaction steps. A sensitivity study of the fuel production rates on various operating parameters

was performed including pressure during reduction, temperature during oxidation, oxidant mole
fraction or oxidant gas flow-rate.

- Both CO<sub>2</sub> and H<sub>2</sub>O splitting were investigated to assess the influence of the oxidizing gas. In addition,

550 co-feeding of H<sub>2</sub>O and CO<sub>2</sub> for direct syngas production was also considered.

- Material cyclability was checked over several consecutive cycles for splitting CO<sub>2</sub> and H<sub>2</sub>O to

552 demonstrate performance stability.

553 - The amount of loaded material in the reactor was optimized to maximize the fuel production capacity.

- Remarkably high fuel production rates and yields were obtained thanks to the methods employed to

improve materials and solar thermochemical conversion outcomes.

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Table 6. Solar-to-fuel efficiency calculations with high load of ceria foams in the solar reactor.

Cycle #	F <sub>fuel</sub> (mL/g.min)	F <sub>fuel</sub> (mol/s)	HHV <sub>fuel</sub> (kJ/mol)	P <sub>solar</sub> (W)	η <sub>solar-to-fuel</sub> (%)
Cycle 1""	7.1	385.10 <sup>-6</sup>	283	1078.1	10.1
Cycle 2"	6.9	374.10 <sup>-6</sup>	283	1078.6	9.8
Cycle 3‴	3.2	174.10 <sup>-6</sup>	286	1113.0	4.5
Cycle 4"'	3.4	184.10 <sup>-6</sup>	286	1079.9	4.9

559

# 560 **4.** Conclusion

561 A complete study was reported ranging from the synthesis of reactive materials in the form of 562 customized foams with a porous structure in the struts, to their application in a two-step solar 563 thermochemical process for fuel production, with optimization of the process conditions and solar 564 reactor operation. Dual-scale porous ceria foams (10 ppi reticulated foams with micrometer-scale 565 pores inside struts) were synthesized and employed in a solar cavity reactor for  $CO_2$  and  $H_2O$ 566 thermochemical splitting. Optimization of cycling parameters and reactor operation was performed to 567 maximize the fuel productivity and efficiency with the customized redox-active material in the form of 568 reticulated porous structure. More than 20 cycles were carried out to optimize fuel production 569 performance based on several experimental parameters such as total pressure, temperatures, oxidant 570 content or gas flowrates. Stable cycling performance for consecutive  $H_2O$  and  $CO_2$  splitting was 571 demonstrated. The on-sun experiments revealed enhanced fuel production rates and yields with high 572 performance stability. Maximum CO and  $H_2$  production yields of 332 µmol/g and 281 µmol/g were 573 obtained after a reduction step at 1400°C under a reduced total pressure of 100 mbar. Peak rates of 574 10.2 mL/min.g and 3.0 mL/min.g were measured during CO and  $H_2$  production steps, respectively. 575 Lower H<sub>2</sub> production rates were evidenced due to the lower steam content compared to the case of 576 CO<sub>2</sub> injection (pure CO<sub>2</sub> was used). This explains the lower production rates obtained when feeding 577 steam instead of CO<sub>2</sub>. Solar syngas production was further evidenced by a simultaneous CO<sub>2</sub> and H<sub>2</sub>O 578 dissociation. Precise tuning of syngas composition remains however challenging given the difficulty to 579 perfectly synchronise gases injection when co-feeding H<sub>2</sub>O and CO<sub>2</sub>. Finally, high loading of ceria foams 580 in the solar reactor enabled to increase the amount of both CO and H<sub>2</sub> produced per cycle (667 mL and 581 513 mL, respectively) with fairly good solar-to-fuel efficiencies at lab-scale (10.1% and 4.9%, 582 respectively). This work demonstrates that solar fuels production can be enhanced by using custom-583 made ceria foams under real solar conditions, thus opening the road towards efficient solar 584 thermochemical processes competing favourably with conventional electrochemical processes.

585

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