



HAL
open science

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

Alex Le Gal, Martin Drobek, A. Julbe, Stéphane Abanades

► **To cite this version:**

Alex Le Gal, Martin Drobek, A. Julbe, Stéphane Abanades. Improving solar fuel production performance from H₂O and CO₂ thermochemical dissociation using custom-made reticulated porous ceria. *Materials Today Sustainability*, 2023, 24, pp.100542. 10.1016/j.mtsust.2023.100542 . hal-04251833

HAL Id: hal-04251833

<https://hal.science/hal-04251833v1>

Submitted on 20 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Improving solar fuel production performance from H₂O and CO₂

2 thermochemical dissociation using custom-made reticulated porous

3 ceria

4 Alex Le Gal¹, Martin Drobek², Anne Julbe², Stéphane Abanades^{1*}

5
6 ¹ Processes, Materials and Solar Energy laboratory (PROMES-CNRS) ; 7 rue du Four Solaire ; 66120 Odeillo Font-Romeu ;
7 France

8 ² Institut Européen des Membranes (IEM) ; CNRS, ENSCM, Univ Montpellier ; Place Eugène Bataillon ; 34095
9 Montpellier ; France

10 * Corresponding author: stephane.abanades@promes.cnrs.fr

11 12 13 **Abstract**

14 Thermochemical CO₂- and H₂O-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 H₂/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 μmol of H₂ and 332 μmol of CO per gram of material during oxidation below
23 1000°C under cooling with a maximum production rate of 3.0 mL/min.g and 10.2 mL/min.g,
24 respectively. Direct syngas production was also evidenced during on-sun experiments with
25 simultaneous H₂O- and CO₂-splitting, which yielded a H₂:CO ratio ranging from 0.7 to 1.14. The dual-

26 scale porous ceria structures were characterized by XRD, SEM, and TGA to confirm material thermal
27 stability during cycling. Finally, optimization of fuel production capacity was achieved by maximizing
28 the total amount of ceria foam loaded into the reactor, yielding 667 mL of CO (409 $\mu\text{mol/g}$) and 513
29 mL of H₂ (314 $\mu\text{mol/g}$) per cycle. A maximum solar-to-fuel efficiency of 10.1% was calculated for CO₂-
30 splitting versus 4.9% for H₂O-splitting cycle. This study thus demonstrated noteworthy fuel production
31 performance in an efficient monolithic reactor under real concentrated solar radiation, from highly-
32 reactive customized ceria foams.

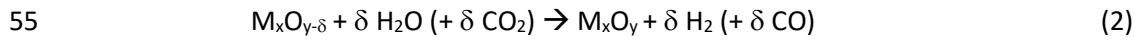
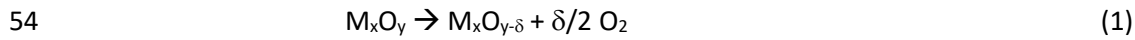
33 **Keywords:** *Hydrogen, Syngas, Water splitting, CO₂ conversion, Thermochemical cycles, Concentrated*
34 *solar energy, Ceria foam.*

35

36 1. Introduction

37 The sustainable production of hydrogen or syngas (H₂+CO mixture) fuel is a major challenge for today's
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
44 overall energy conversion performance due to low power generation efficiency. Alternative solutions
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 H₂O and/or CO₂ have been investigated for several decades,
50 as reported in numerous review papers [6]-[10]. The thermochemical process involves redox pairs to

51 dissociate H₂O (or CO₂) molecules into separate streams of H₂ (or CO) and O₂. These cycles are
52 composed of an activation step, consisting of the partial metal oxide reduction (Eq. 1), followed by a
53 hydrolysis step leading to the release of H₂ (or CO) (Eq. 2).



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

63 Currently, the measured performance of such processes is still low ($\eta_{\text{solar-to-syngas}}$ below 5%, defined as
64 the ratio of the higher heating value of the syngas produced to the sum of solar energy input Q_{solar} and
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 CeO₂, NiFe₂O₄ or lanthanum-manganite perovskites La_xSr_{1-x}MnO₃) lead
75 to low reduction capability or limited hydrogen or syngas production output per cycle. These fuel

76 production performances could be increased by using either new materials with improved redox
77 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 CO₂ 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)O_x [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 H₂ 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 fibers
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_2O 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_2/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,

128 temperature during oxidation, oxidant mole fraction or oxidant gas flow-rate (Sections 3.2.1 and 3.2.2).
 129 Operational strategies can thus be optimized by focusing on tuning these parameters. Processing
 130 limitations regarding the simultaneous co-feeding of H₂O and CO₂ for direct syngas production were
 131 also unravelled (Section 3.2.3). The amount of loaded material in the reactor was finally optimized for
 132 maximum fuel production capacity (Section 3.3). Results were compared to the best-in-class materials
 133 in order to confirm that solar fuel production performance can be improved by a relevant material
 134 shaping, while optimizing its total loaded amount and cycling conditions.

135 2. Experimental methods

136 2.1. Materials synthesis

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

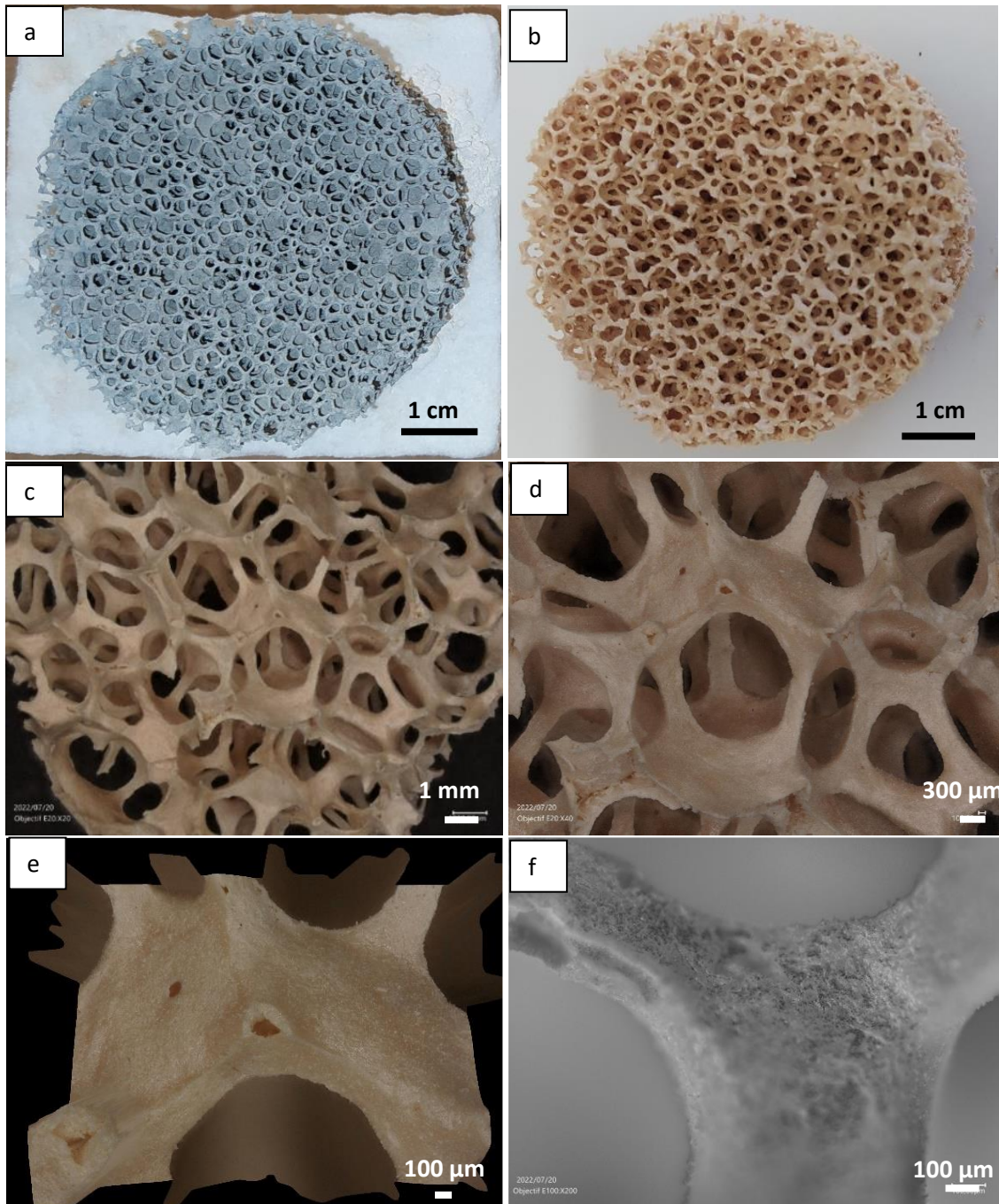
140 *Table 1. Components in the slurry used to make foams via the replication method (the percentages*
 141 *are expressed in relation to the mass and volume of ceria).*

| Slurry components | Name/composition/provider | Proportion |
|-------------------|--|------------|
| Raw material | Ceria (Sigma-Aldrich, 99.9%, <5 μm powder) | m |
| Solvent | Water | m/3 |
| Porogen | Carbon fibbers (Sigrafil® M80-3.0, filaments 7 μm diameter and 80 μm long) | 30 vol% |
| Binder | Polyvinyl alcohol (Mowiol) | 1.35 wt% |
| Dispersant | Dolapix (Zschimmer & Schwarz GmbH) | 0.85 wt% |

142 Then, a sacrificial polyurethane template (interconnected open-cell foam with a pore density of 10 ppi)
 143 was plunged once into the slurry and dried overnight at room temperature. The as-impregnated foam
 144 was then slowly heated up to 1000°C (at 2.5°C/min) to remove the organic components of the foam
 145 precursor, and annealed at 1400°C during 3 hours to achieve sintering that provides a mechanical
 146 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 CeO₂
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/cm³. By comparison with the density of ceria ($\rho = 7.13$
162 g/cm³ – *data from Sigma-Aldrich*), a porosity of 85% is calculated.

163



164

165

166

167

168

169

170

171

172

173

Figure 1. Images of porous CeO₂ 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 CeO₂ 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 α radiation ($\lambda_{Cu} = 0.15406$ nm, angular range = 20-80°, 2 θ , 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
182 S4800) was used to observe the microstructure of ceria foams before and after thermochemical cycles.

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 CO₂-splitting step) and CO₂ was injected
189 during the oxidation step (50% CO₂ in Ar with a CO₂ 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, $p_{O_2} = 10^{-5}$ 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. CO₂ (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 O₂ trace analyser (electrochemical cell) and an H₂ analyser (catharometer)
209 or CO analyser (NDIR sensor) to measure gas concentrations on-line. When co-feeding H₂O and CO₂, a
210 syngas analyser (Emerson XStream) is used to monitor the gas species concentrations continuously
211 and simultaneously (especially H₂ 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.

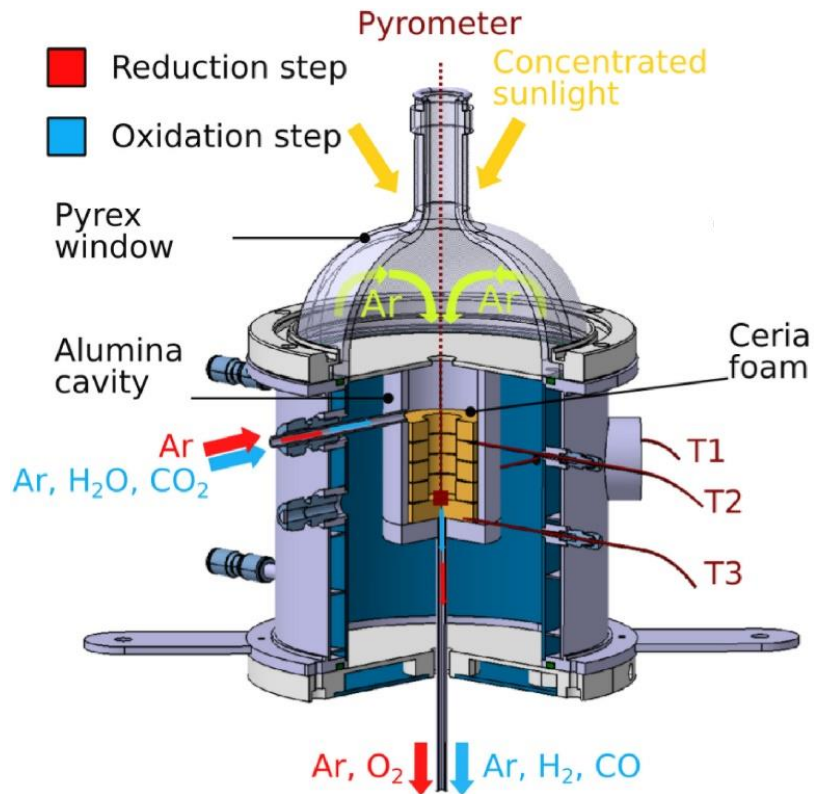
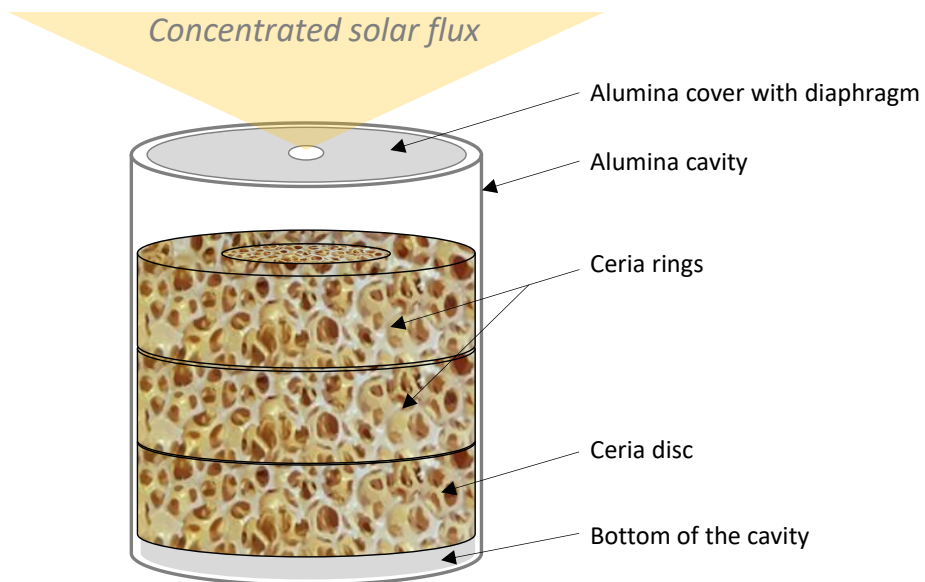


Figure 2. Scheme of the solar reactor.

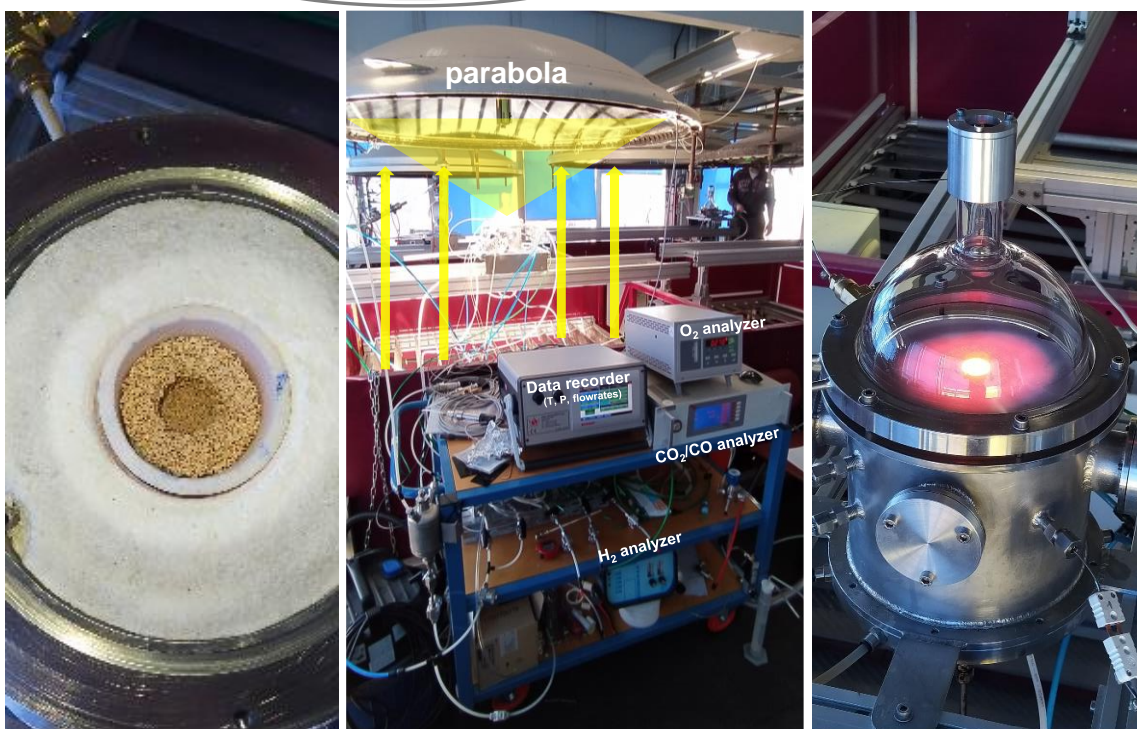
221
222

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 (p_{O_2} 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 ($T_1 = 1400^\circ\text{C}$). 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_2 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_{solar} 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_{O_2})
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_2 flows are regulated to the desired values by
247 using mass flow meters. H_2/CO concentrations in the exhaust gas are recorded on-line and integrated
248 over time to calculate the total H_2/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.



251



252

253

Figure 3. Schematic representation of ceria foams placed in the cavity (top) and pictures of the solar reactor used to characterize the H₂/CO production (bottom).

254

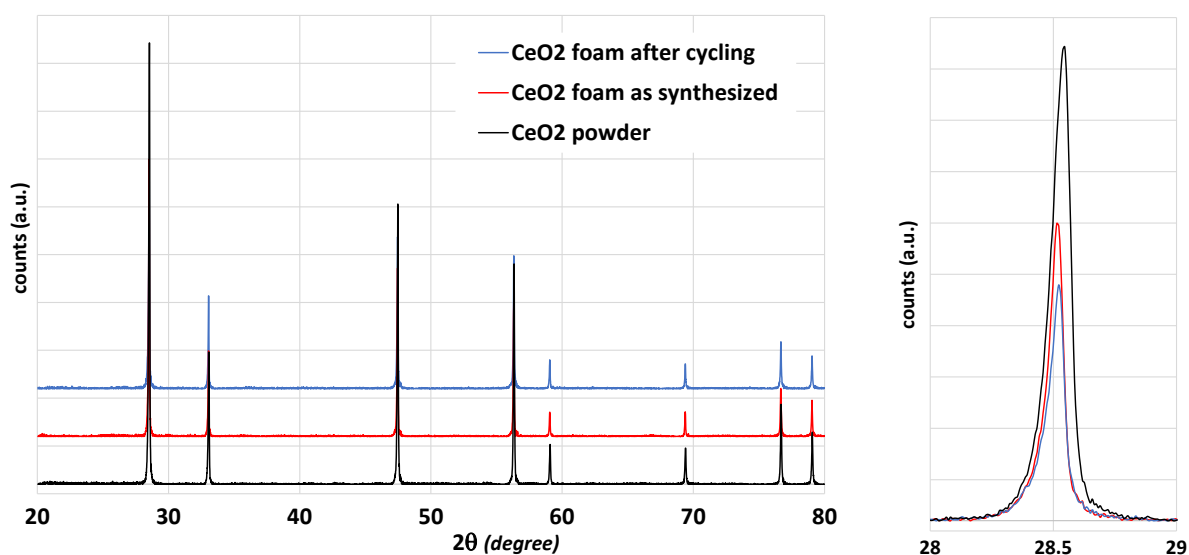
255

256 3. Results and discussion

257 3.1 Preliminary characterizations of materials

258 XRD patterns of the crushed foams before and after cycling are presented in Figure 4. The ceria phase
259 is observed and compared to pure ceria powder. The diffraction peaks are sharpened indicating an

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

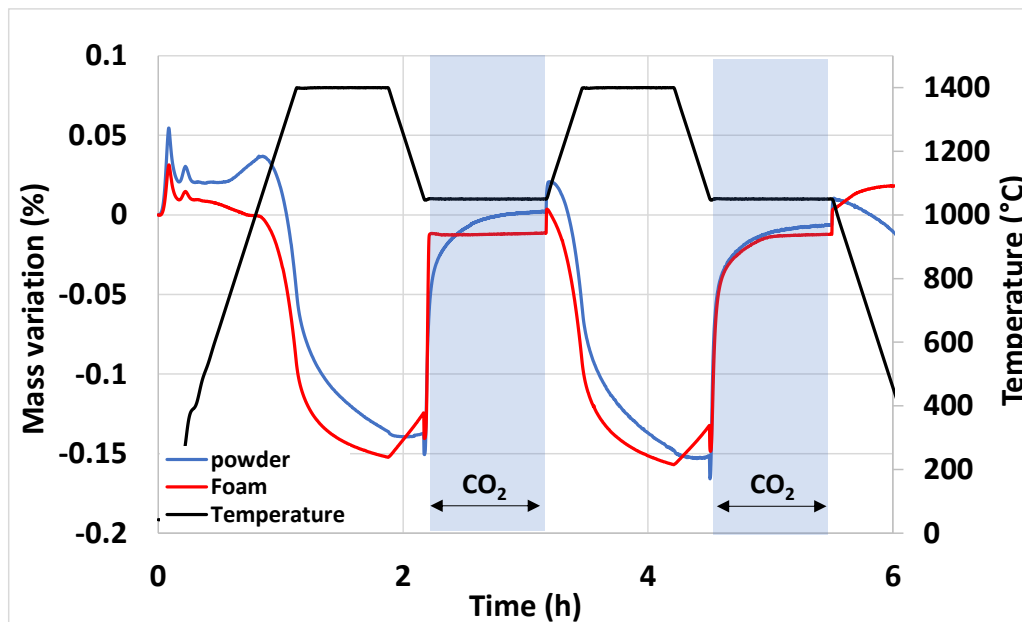


266

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

268 *(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 CO₂-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 μmol/g of O₂ and the ceria foam released 47 and 51 μmol/g of
273 O₂. The CO production yields were 94 and 98 μmol/g with the ceria powder, and 99 and 96 μmol/g
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 CO₂ splitting.



277

278 *Figure 5. TGA of the commercial ceria powder and derived custom-made foam during two consecutive*
 279 *CO₂-splitting cycles.*

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

284

285 *3.2 Parametric study with the CeO₂ foams in the solar reactor*

286

287 A parametric study was carried out with the aim of optimizing the production performance of solar
 288 fuel (H₂/CO). Consecutive cycles of CO₂ and H₂O dissociation were performed to study the effect of
 289 various operating conditions on fuel production rates and yields. The reduction temperature was set
 290 at 1400°C (T₁) and the parametric study focused on various parameters including the pressure of the
 291 reduction step (P_{red}), the temperature of the oxidation step (T_{ox}), the total gas flowrate during oxidation
 292 (Q_{ox}), and the reactive gas concentration (CO₂/H₂O).

293

3.2.1 CO₂ dissociation cycles

294 Two series of CO₂-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 (O₂ and CO). Note that gas rates are scaled with two different axes, otherwise
299 the O₂ 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 O₂ 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 CO₂ 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 ($Q_{Ar,cavity}=0.2$ 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 δ , 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.

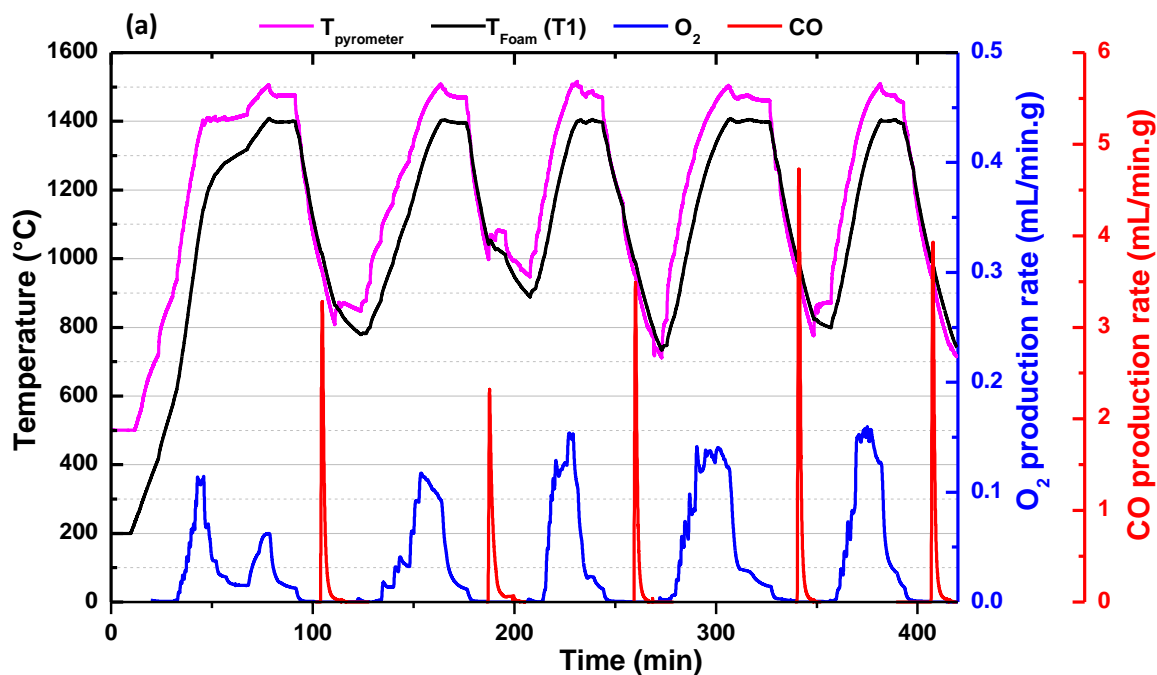
313 Table 2 reports the results of CO₂ splitting cycles for each experimental condition. During the three
314 first cycles, the O₂ production yield reached 97, 100, and 99 $\mu\text{mol/g}$ ($\delta \sim 0.034$) for a total pressure of
315 870 mbar (atmospheric pressure in Odeillo laboratory in Pyrenees mountains) during the reduction
316 step. This reduction yield was well reproducible during cycles #1, #2, and #3, all carried out under the
317 same experimental conditions ($Q_{Ar}=1.2$ NL/min, $T_{red}=1400^\circ\text{C}$). Since the controlled temperature (T1)
318 was located near the foam bottom, the upper part of the material was actually above this temperature
319 (as denoted by the pyrometer measurement). Due to this temperature gradient, the global reduction

320 yield was higher than the one measured in TGA. The associated CO production yield, with CO₂ injection
321 starting at 1000°C during cooling, was 245, 229, 226 μmol/g for cycle #1, #2, #3 with peak production
322 rates of 3.3, 2.3, and 3.5 mL/min.g, respectively. The lower peak production rate during cycle #2 is due
323 to a lower cooling rate during the oxidation step, as observed in Figure 6. These production rates and
324 yields are consistent with previously reported values for ceria foams [36].

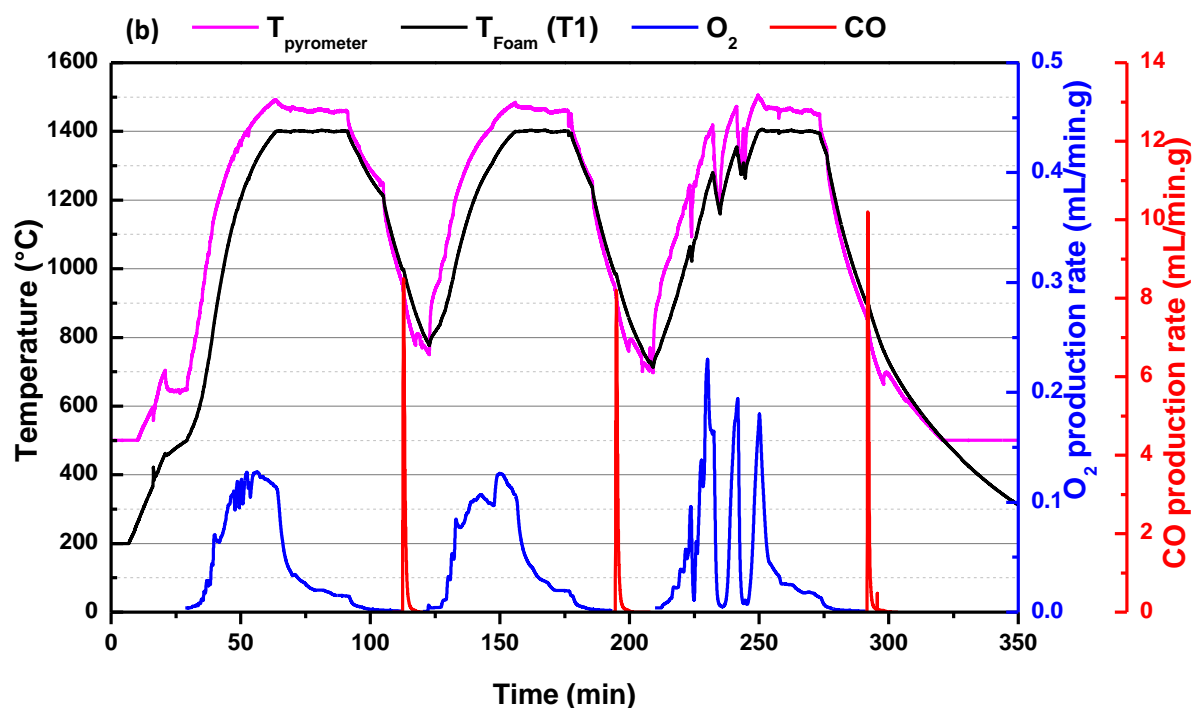
325 By decreasing the total pressure during the reduction step at 292 mbar (cycle #5) and 103 mbar (cycle
326 #4), the oxygen partial pressure was decreased and the O₂ yield was significantly improved up to 123
327 μmol/g ($\delta \sim 0.042$) and 151 μmol/g ($\delta \sim 0.052$) respectively, while the associated CO production yields
328 reached 271 μmol/g and 321 μmol/g, respectively. The CO peak production rate was also improved
329 (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 CO₂ (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 μmol/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 CO₂ 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 CO₂ 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 CO₂ injection
337 temperature of 1000°C (cycles #6) and 10.2 mL/min.g for an injection temperature of 900°C (cycle #8).

338



339



340

341 Figure 6. Temperature profiles and gas production rate evolution during CO₂-splitting solar cycles with

342 CeO₂ foams: (a) cycles #1-5: influence of P_{red} ($T_{ox} < 1000^{\circ}C$ and CO₂ flowrate = 1 NL/min), (b) cycles #6-

343

8: influence of T_{ox} ($P_{red} = 100$ mbar and CO₂ flow rate = 2 NL/min).

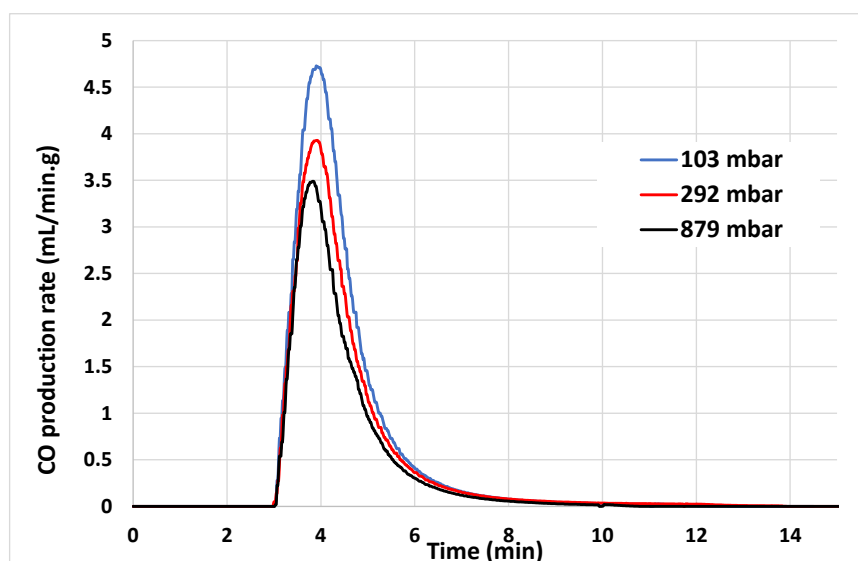
344

345 Table 2. Experimental conditions and results of CO₂-splitting solar cycles with CeO₂ foams (*m* = 50.02

346 g).

| Cycle # | Reduction pressure (mbar) | CO ₂ flowrate (NL/min) | Oxidation temperature start (°C) | O ₂ yield (μmol/g _{Ceria}) | CO yield (μmol/g _{Ceria}) | CO peak production rate (mL/min.g) | CO/O ₂ 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
348 This experimental study demonstrates the relevant cyclability of ceria foams, thus offering good
349 repeatability of CO production. Favourable conditions for increasing CO production are a decrease in
350 total pressure during the reduction step (decrease of p_{O_2}), an increase in CO₂ flowrate and a decrease
351 of re-oxidation temperature. Such conditions enhance CO production but can have a negative impact
352 on energy efficiency as (i) higher gas flowrates result in higher energy consumption for heating, (ii) a
353 reduction step at low pressure implies pumping work, and (iii) lowering the temperature during the
354 oxidation step results in sensible heat losses when considering the full cycle.



355
356 Figure 7. CO production rate evolution for three different total pressures during the reduction step
357 (cycles #3-5, $T_{ox} < 1000^{\circ}C$, 1 NL/min CO₂ flowrate)

358

3.2.2 Water dissociation cycles

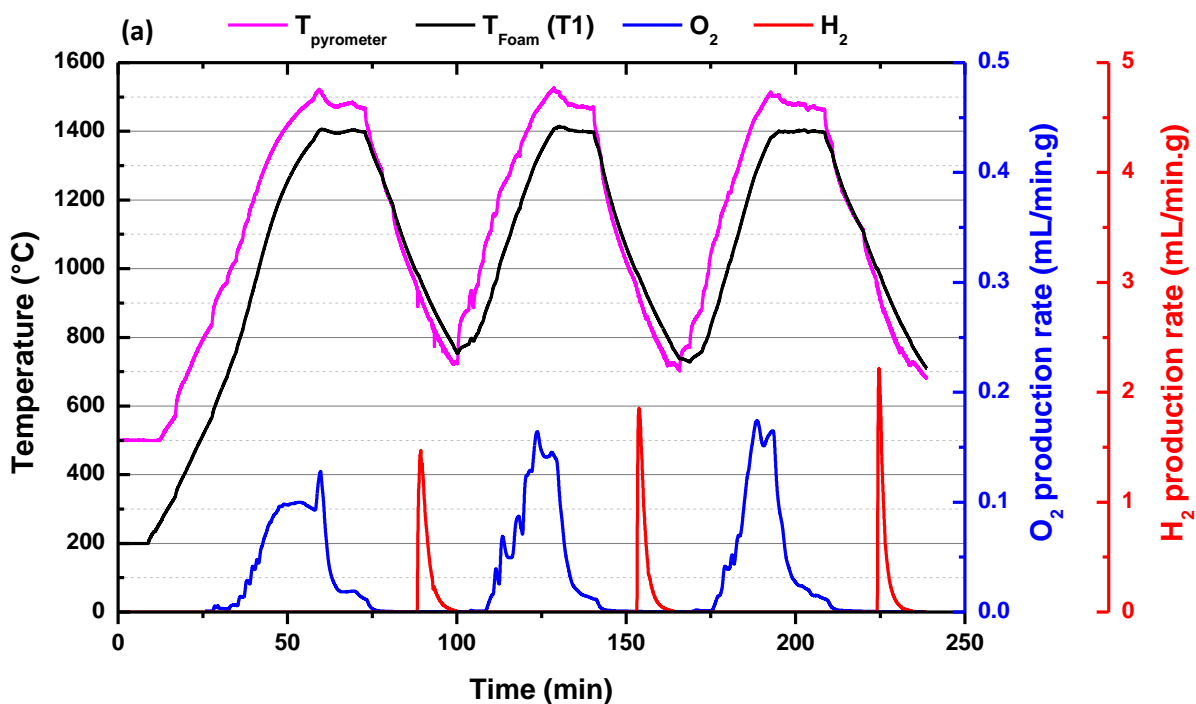
359 Two series of H₂O-splitting solar cycling experiments were also realized with the same foams (total
 360 loaded mass $m = 50.02$ g). Several experimental parameters were investigated such as the total
 361 pressure during reduction, the total Ar carrier gas flowrate during hydrolysis, and the steam content.
 362 Table 3 presents the selected experimental conditions for the reduction and oxidation steps, as well
 363 as the results of O₂ and H₂ production. Figure 8 shows the temperature profiles and gas production
 364 rates during the 8 thermochemical cycles.

365 *Table 3. Experimental conditions and results of H₂O-splitting solar cycles with CeO₂ foams ($m = 50.02$ g).*

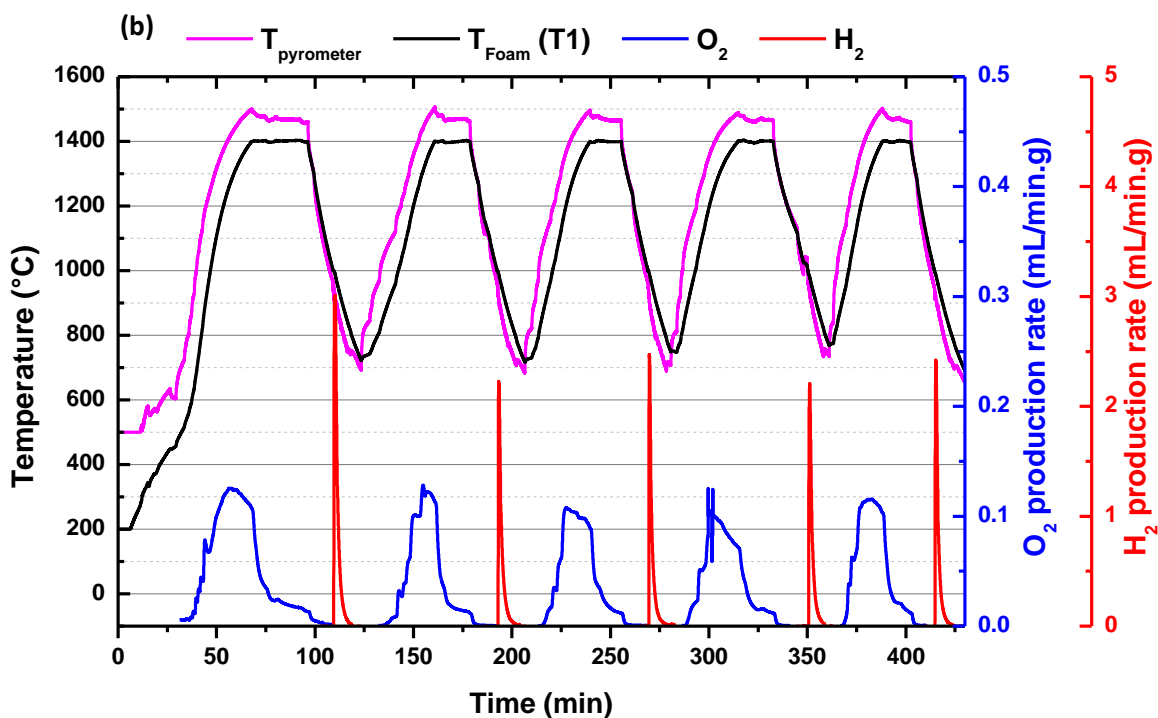
| Cycle # | Reduction pressure (mbar) | Argon flowrate (hydrolysis-NL/min) | H ₂ O mole fraction | O ₂ yield ($\mu\text{mol/g}_{\text{ceria}}$) | H ₂ yield ($\mu\text{mol/g}_{\text{ceria}}$) | H ₂ peak production rate (mL/min.g) | H ₂ /O ₂ ratio |
|-----------------|---------------------------|------------------------------------|--------------------------------|---|---|--|--------------------------------------|
| 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 |

366

367



368



369

370 Figure 8. Temperature profiles and gas production rate evolution during H_2O -splitting solar cycles

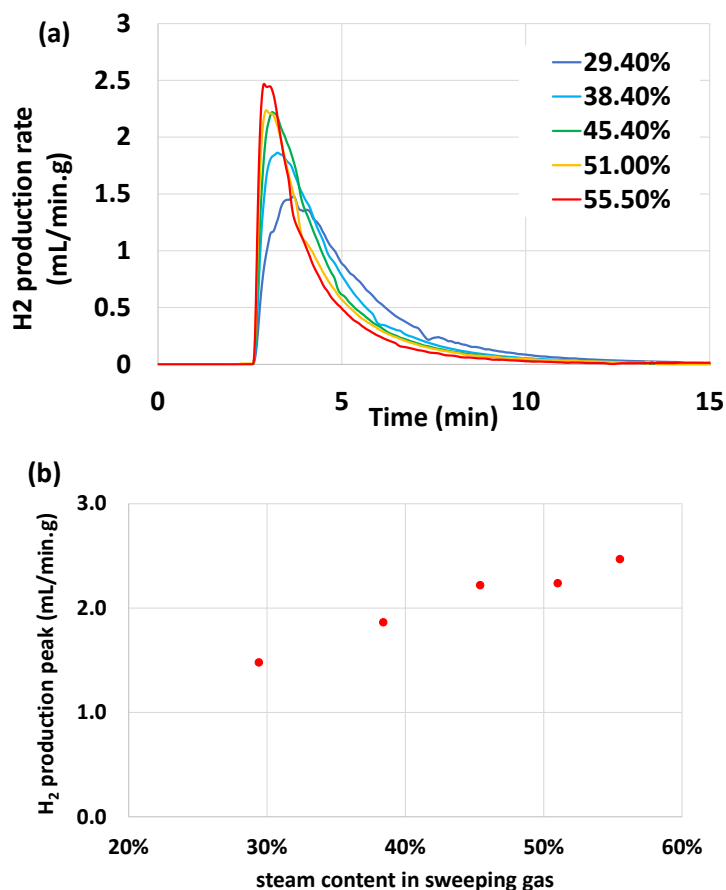
371 with CeO_2 foams: (a) cycles #1'-3': influence of H_2O mole fraction, (b) cycles #4'-8': influence of

372 reduction pressure (P_{red}) and Ar flow rate during oxidation.

373

374 The highest H₂ production yield was 280.6 μmol/g_{ceria} 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 H₂ production rate was 3.0 mL/min.g_{ceria} that was obtained during the same cycle. This peak
377 rate is lower than in the case of CO₂ because pure CO₂ was used, whereas Ar was used as carrier gas
378 during H₂O injection, which lowered the steam content in the oxidation step. The optimal parameters
379 to improve the H₂ 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 H₂
384 peak production rate. The steam content only impacts the hydrolysis rate while overall O₂ and H₂ 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 H₂O mole fraction but this
387 effect does not impact H₂ 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 H₂ (thereby shifting the
389 reaction equilibrium towards H₂), and further sweeps the H₂ produced away from the reaction sites,
390 which in turn promotes the hydrolysis reaction.

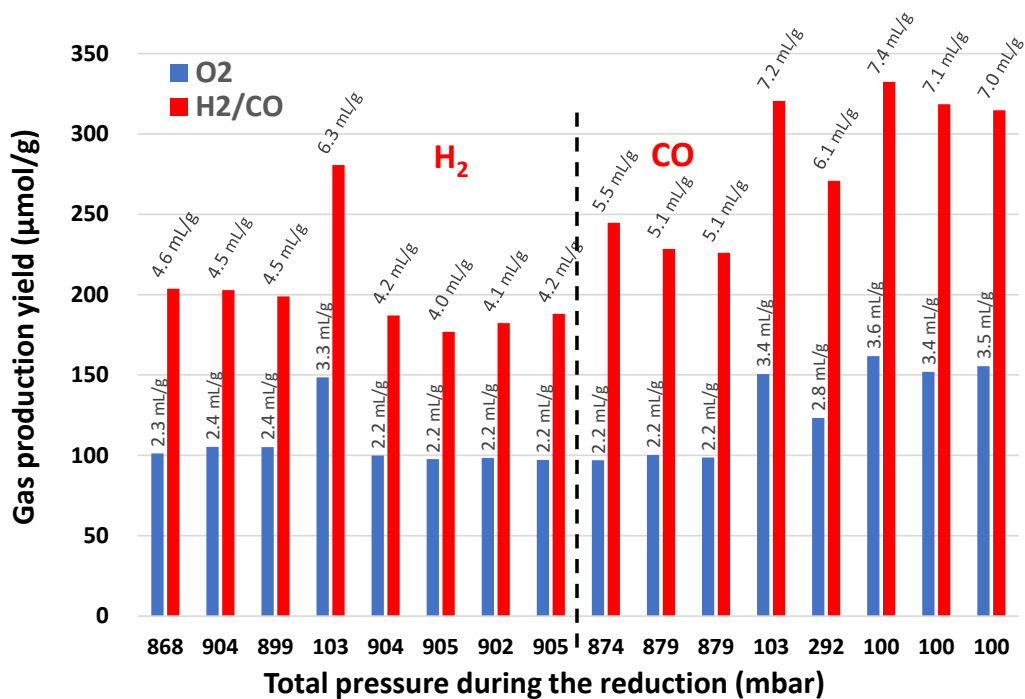


391

392

393 *Figure 9. (a) H₂ production rate evolution and (b) peak production rate as a function of steam content*
 394 *in the sweep gas (cycles #1', 2', 3', 5', 6': reduction step at T₁ = 1400°C and other hydrolysis*
 395 *parameters unchanged).*

396 Figure 10 compares the production yields of CO and H₂ by solar thermochemical cycles with ceria foams
 397 over the entire solar experimental series. The cycling capability is highlighted as no deactivation was
 398 observed regarding O₂ release during the reduction steps. About 100 μmol/g of O₂ was released during
 399 reduction steps at T₁ = 1400°C under a total pressure of ~900 mbar. The dissociation of CO₂ appears to
 400 be more efficient than H₂O splitting, which is mainly the result of the different concentration of oxidant
 401 gas during the oxidation step. Indeed, a pure CO₂ stream was used while no experiment could be
 402 conducted with pure steam injection due to technical constraints.



403

404 *Figure 10. Comparison of O₂ and CO/H₂ production yields during 16 consecutive solar thermochemical*
 405 *cycles using ceria foams and different experimental conditions.*

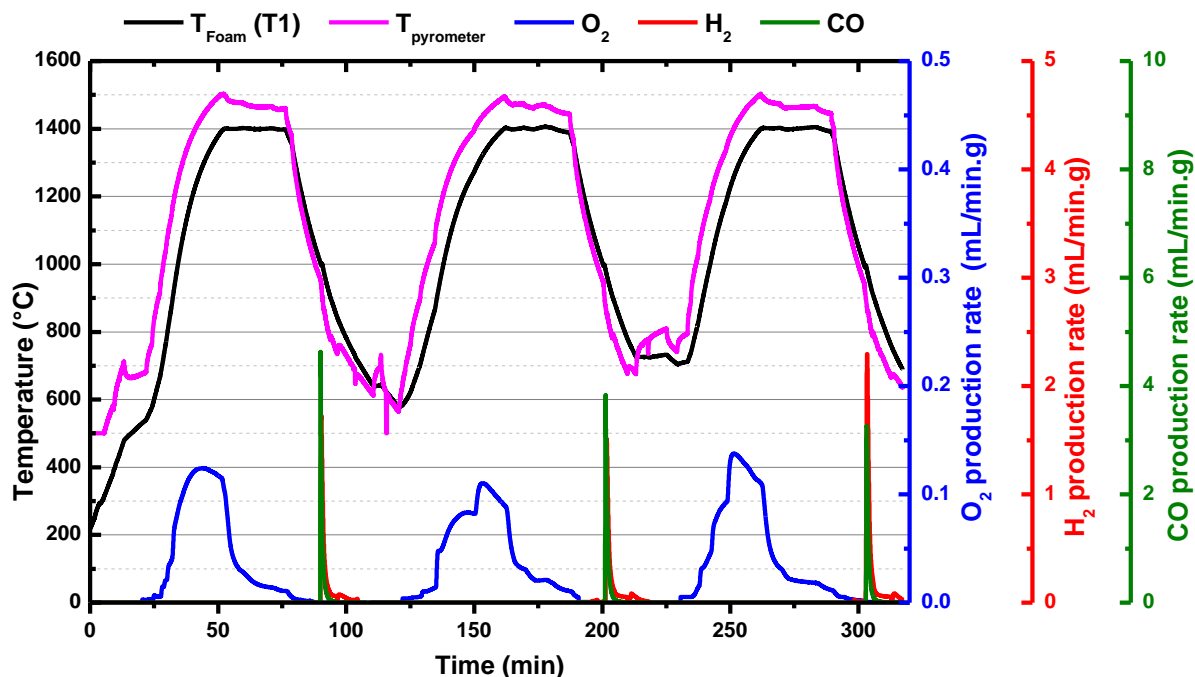
406

407 3.2.3 Simultaneous H₂O and CO₂ dissociation cycles for syngas production

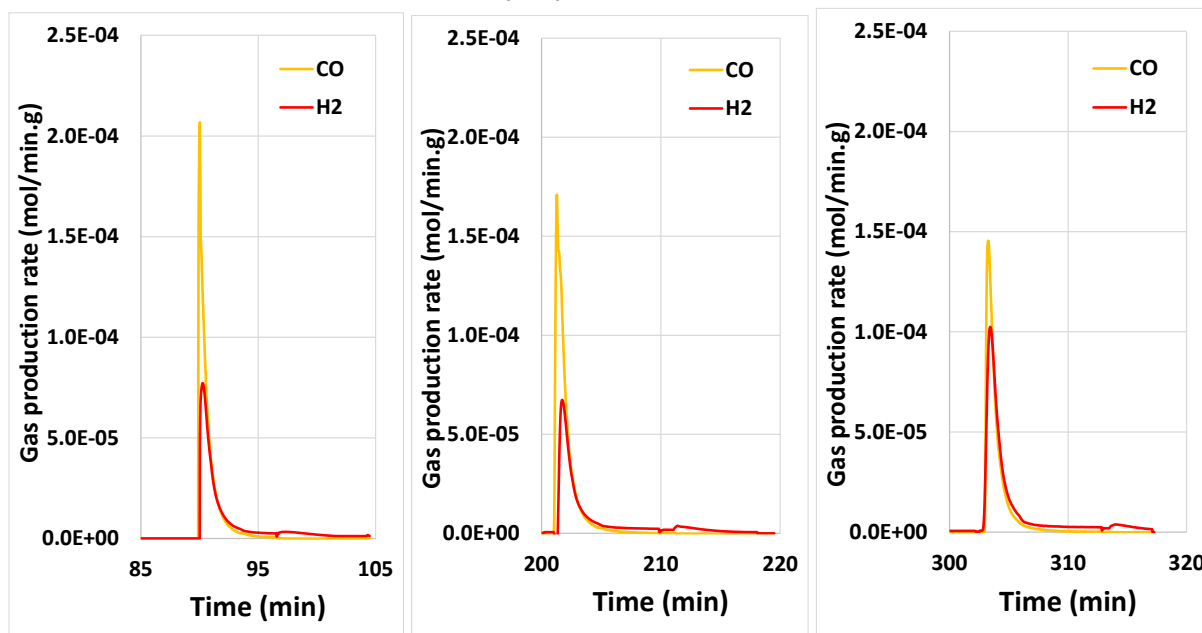
408 In order to complete the on-sun experimental campaign with ceria foams, simultaneous CO₂- and H₂O-
 409 splitting cycles were performed to produce syngas. The reduction steps were carried out under low
 410 pressure (115 mbar) with a flow of Ar (1.2 NL/min), and the oxidation steps were carried out at
 411 T_{ox}<1000°C with 41% steam (50 g/h), 39% CO₂ (1 NL/min), and 20% Ar (0.5 NL/min) as sweep gas
 412 composition (Table 4). Steam and CO₂ 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
 414 consecutive splitting cycles were performed and Figure 11 shows the temperature profiles and gas
 415 production rates. The maximum production rate of CO was higher than H₂ 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).

417

418



419



420

421 *Figure 11. Temperature profiles and gas production rate evolution during simultaneous CO₂- and H₂O-*

422 *splitting solar cycles with CeO₂ foams: (top) overall successive cycles, (bottom) zoom on CO and H₂*

423 *production peaks (cycles #1"-3").*

424

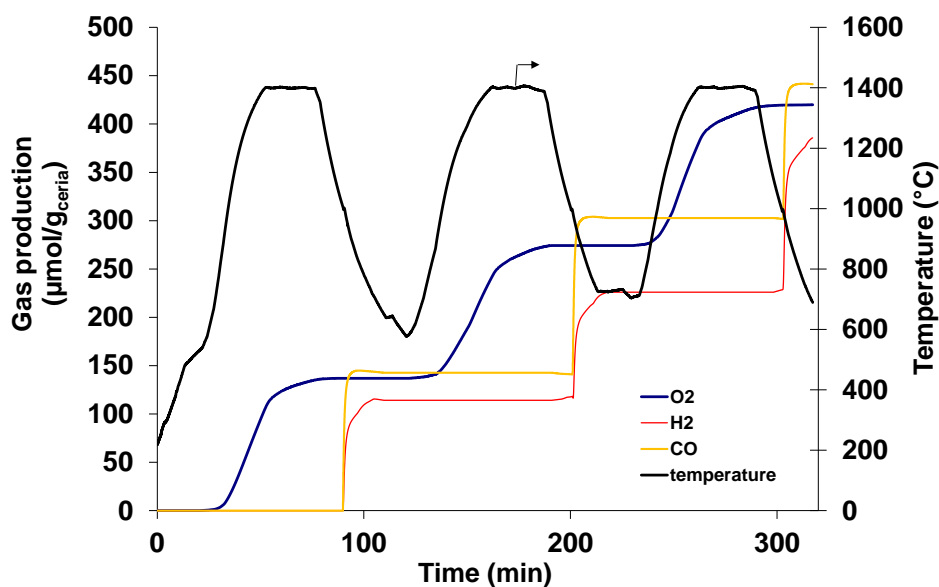
425 Figure 12 shows the cumulative production yields of O₂ during the reduction steps and of CO and H₂

426 during the reoxidation steps. The O₂ 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 H₂ production yield (144.6 and
 429 160.7 μmol/g for CO against 114.7 and 111.9 μmol/g for H₂). In contrast, during the third cycle, the
 430 production of H₂ was higher than the production of CO (159.0 and 138.5 μmol/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 H₂O and CO₂ 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 H₂O and CO₂ for H₂:CO ratio control. Direct syngas production by
 437 co-feeding of H₂O and CO₂ did not turn to be advantageous for precise control of the syngas
 438 composition. Nevertheless, the sum of CO and H₂ production yields lead to full reoxidation extent with
 439 a (CO+H₂/O₂) ratio equal to 1.9 or 2.

440



441

442 *Figure 12. Cumulative gas production evolution (O₂ and syngas) and temperature profile for three*
 443 *consecutive thermochemical cycles operated on-sun with CeO₂ porous foams*

444

445 *Table 4. Results of simultaneous CO₂- and H₂O-splitting solar experiments with CeO₂ foams (m = 64.1*
 446 *g).*

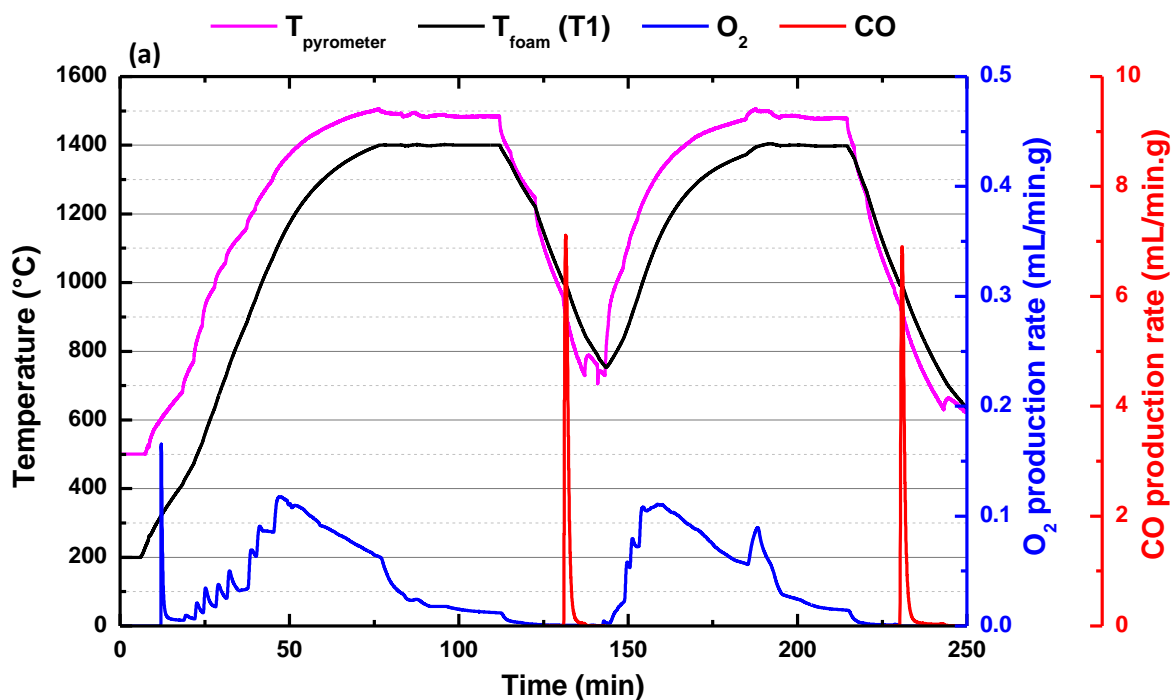
| Cycle # | O ₂ ($\mu\text{mol/g}_{\text{ceria}}$) | CO yield ($\mu\text{mol/g}_{\text{ceria}}$) | CO maximum production rate (mL/g.min) | H ₂ yield ($\mu\text{mol/g}_{\text{ceria}}$) | H ₂ maximum production rate (mL/g.min) | CO + H ₂ ($\mu\text{mol/g}_{\text{ceria}}$) | (CO+H ₂)/O ₂ |
|------------------|--|--|---|--|---|---|-------------------------------------|
| 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

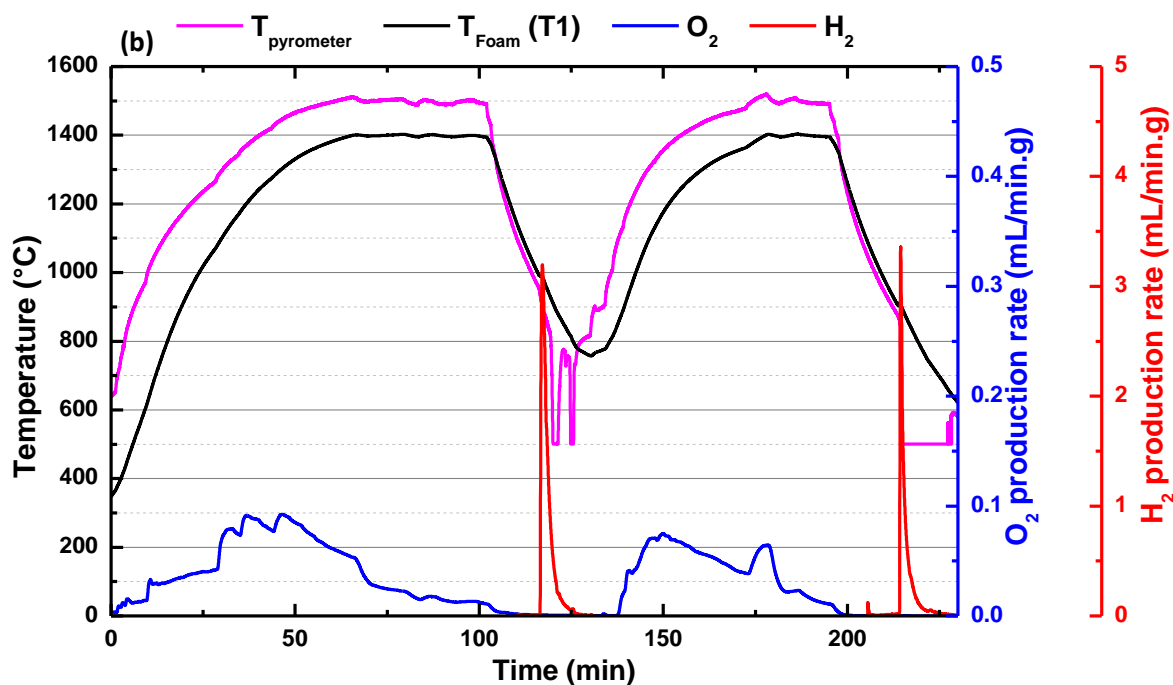
448 *3.3 Effect of total loaded mass of ceria foams*

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 CO₂ 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% CO₂ gas flowing into the cavity (2 NL/min CO₂
 457 and 1 NL/min Ar). In addition, two H₂O splitting cycles were carried out with low-pressure during
 458 reduction first (105 mbar) and atmospheric pressure (900 mbar). The oxidation steps were operated
 459 at T_{ox}<1000°C and T_{ox}<900°C with 60 g/h H₂O and 1 NL/min Ar.

460



461



462

463 *Figure 13. Temperature profiles and gas production rate evolution during (a) CO₂-splitting and (b)*

464 *H₂O-splitting solar cycles with maximized loading of CeO₂ foams (m = 72.9 g) in the solar reactor.*

465 Table 5 presents the O₂ and CO/H₂ yields produced during these cycles. The quantities of O₂ produced

466 during the reduction steps were higher than the previous values measured under the same conditions

467 (212.5, 198.9, and 198.1 μmol/g at 105 mbar and 116.0 μmol/g at 900 mbar). The δ values were thus

468 also higher (maximum δ ~ 0.073 in cycle #1'''). 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 $\mu\text{mol/g}$ during the
 474 oxidation steps (representing 9.1 and 9.0 mL/g) and the H₂ production yields reached 314.3 and 204.8
 475 $\mu\text{mol/g}$. These amounts of CO and H₂ overpass the previous values measured under the same
 476 conditions, which were respectively 332.3 $\mu\text{mol/g}$ (cycle #6 in Table 2) and 280.6 $\mu\text{mol/g}$ (cycle #4' in
 477 Table 3 at low pressure and $T_{\text{ox}} < 1000^\circ\text{C}$). The CO:O₂ ratio was 1.9 and 2.0, which confirms a total re-
 478 oxidation of the reduced ceria by CO₂, whereas the H₂:O₂ 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 CO₂ 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 H₂ 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.

487

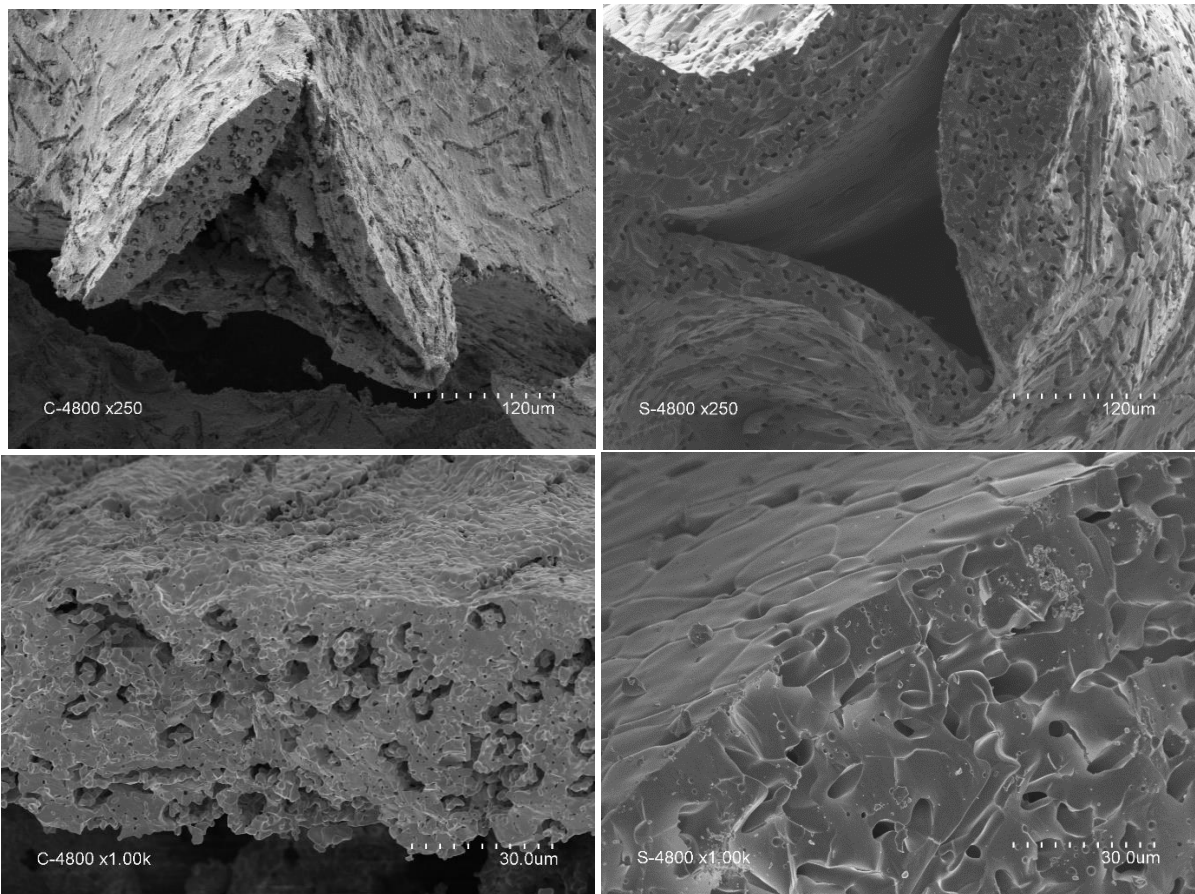
488 *Table 5. Results of CO₂- and H₂O-splitting cycles with 72.9 g of ceria foams in the solar reactor.*

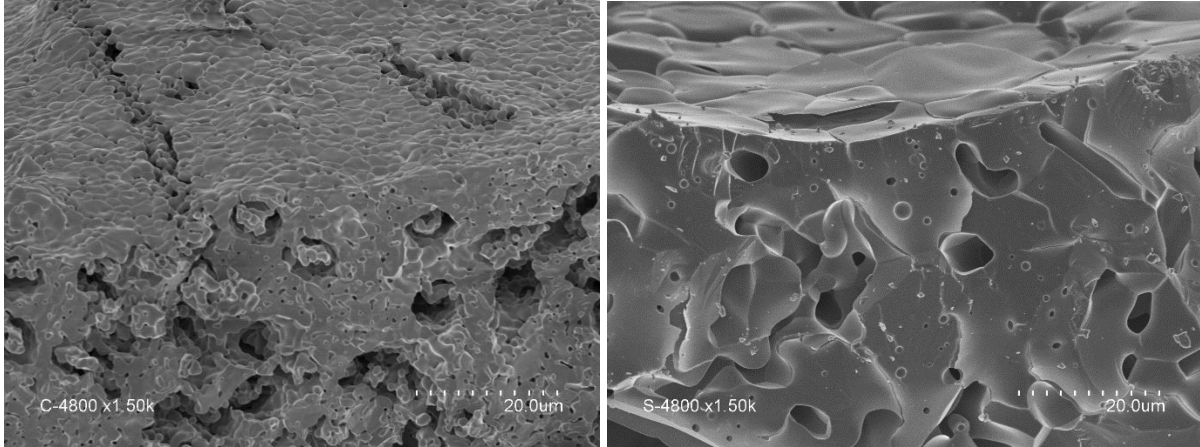
| Cycle # | Reduction pressure (mbar) | CO ₂ or H ₂ O mole fraction | O ₂ ($\mu\text{mol/g}_c$ ceria) | CO ($\mu\text{mol/g}_c$ ceria) | CO maximum production rate (mL/g.min) | H ₂ ($\mu\text{mol/g}_c$ ceria) | H ₂ maximum production rate (mL/g.min) | (CO or H ₂)/O ₂ |
|-------------------|---------------------------|---|---|---------------------------------|---------------------------------------|---|---|--|
| 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 |

489
490
491
492
493
494
495
496
497
498
499

Figure 14 presents SEM pictures of a ceria foam before and after thermochemical cycling under concentrated solar radiations. It is observed that the thickness of ceria strands does not change after thermal cycling (Fig. 14 right). Cylindrical pores of 8 μm diameter and 80 μm long are observed in both cases. Nevertheless, the material seems to slightly densify after thermochemical cycling. The ceria grain size is also increased after thermal cycling (unlike the crystallite size that remains unchanged according to XRD, Fig. 4). The grains grow from 5 μm to 20 μm . A grain can be composed of several crystallites (crystalline domains). Grain growth is observed by SEM due to agglomeration of crystallites. These observations confirm the good thermal stability of the developed porous ceria foams under concentrated solar energy and demonstrate that grain growth has no influence on CO_2 and H_2O splitting rates and yields.

500
501





502
 503 *Figure 14. SEM pictures of a ceria foam before (left) and after (right) the whole series of solar CO₂ and*
 504 *H₂O 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]:

$$507 \quad \eta_{\text{solar-to-fuel}} = F_{\text{fuel}} \cdot \text{HHV}_{\text{fuel}} / P_{\text{solar}} \quad (3)$$

508 where F_{fuel} denotes the CO or H₂ production rate (mol/s), HHV_{fuel} the higher heating value of CO (= 283
 509 kJ/mol) or H₂ (= 286 kJ/mol), and P_{solar} the maximum solar power input during the reduction step (kW).
 510 Such real-time efficiency eliminates the influence of arbitrary process conditions such as the duration
 511 of the reduction step or the effect of weather conditions. Auxiliary power inputs are not taken into
 512 account such as pumping works, inert gas regeneration, solar tracking, etc.

513 P_{solar} 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. CO₂-splitting cycles are more efficient compared to H₂O-splitting cycles with peak solar-to-fuel
 516 efficiencies of 10.1% and 9.8% for CO₂ splitting against 4.5% and 4.9% for H₂O 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 CO₂ splitting in the same reactor ($P_{\text{red}}=110$ mbar, $T_{\text{Ox}}=900^\circ\text{C}$, $Q_{\text{CO}_2}=2$ 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
 521 is strongly dependent (inversely proportional) on the duration of the reduction step which can be

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:

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

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

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

549 - Both CO₂ and H₂O splitting were investigated to assess the influence of the oxidizing gas. In addition,
550 co-feeding of H₂O and CO₂ for direct syngas production was also considered.

551 - Material cyclability was checked over several consecutive cycles for splitting CO₂ and H₂O to
552 demonstrate performance stability.

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

554 - Remarkably high fuel production rates and yields were obtained thanks to the methods employed to
555 improve materials and solar thermochemical conversion outcomes.

556

557

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

| Cycle # | F _{fuel} (mL/g.min) | F _{fuel} (mol/s) | HHV _{fuel} (kJ/mol) | P _{solar} (W) | η _{solar-to-fuel} (%) |
|------------|---------------------------------|------------------------------|---------------------------------|---------------------------|-----------------------------------|
| Cycle 1''' | 7.1 | 385.10 ⁻⁶ | 283 | 1078.1 | 10.1 |
| Cycle 2''' | 6.9 | 374.10 ⁻⁶ | 283 | 1078.6 | 9.8 |
| Cycle 3''' | 3.2 | 174.10 ⁻⁶ | 286 | 1113.0 | 4.5 |
| Cycle 4''' | 3.4 | 184.10 ⁻⁶ | 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 CO₂ and H₂O
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 H₂O and CO₂ splitting was
571 demonstrated. The on-sun experiments revealed enhanced fuel production rates and yields with high
572 performance stability. Maximum CO and H₂ 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 H₂ production steps, respectively.
575 Lower H₂ production rates were evidenced due to the lower steam content compared to the case of
576 CO₂ injection (pure CO₂ was used). This explains the lower production rates obtained when feeding
577 steam instead of CO₂. Solar syngas production was further evidenced by a simultaneous CO₂ and H₂O
578 dissociation. Precise tuning of syngas composition remains however challenging given the difficulty to
579 perfectly synchronise gases injection when co-feeding H₂O and CO₂. Finally, high loading of ceria foams
580 in the solar reactor enabled to increase the amount of both CO and H₂ 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

586 **Acknowledgements**

587 This research was partially funded by H2VERT project led by Région Occitanie in France (Défi clé
588 Hydrogène Vert- Plan de relance - FEDER REACT EU - Hydrosol sub-project). The authors thank Marielle
589 Vallès for her internship contribution in microscopy to this project.

590

591 **References**

592 [1] Lhyfe inaugurates world's first industrial site for renewable green hydrogen, Fuel cells bulletin,
593 2021, 11, 2021

- 594 [2] Rodler A, Haurant P, Faggianelli G, Pigelet G, Poggi P. Combined heat and power generation of the
595 hydrogen chain based on MYRTE platform. Solar World Congress 2015. International Solar Energy
596 Society conference proceedings. 8-12, November 2015
- 597 [3] Funk J E. Thermochemical hydrogen production: past and present, International journal of
598 hydrogen energy, 26, 3, pp.185-190, 2001
- 599 [4] Li X, Sun X, Song Q, Yang Z, Wang H, Duan Y. A critical review on integrated system design of solar
600 thermochemical water-splitting cycle for hydrogen production, International journal of hydrogen
601 energy, 47, 79, pp.33619-33642, 2022
- 602 [5] Yadav D, Banerjee R. A review of solar thermochemical processes, Renewable and sustainable
603 energy reviews, 54, pp.497-532, 2016
- 604 [6] Safari F, Dincer I. A review and comparative evaluation of thermochemical water splitting cycles
605 for hydrogen production, Energy conversion and management, 205, 112182, 2020
- 606 [7] Abanades S. Metal oxides applied to thermochemical water splitting for hydrogen production using
607 concentrated solar energy, Chem Engineering, 3, 63, 2019
- 608 [8] Mao Y, Gao Y, Dong W, Wu H, Song Z, Zhao X, Sun J, Wang W. Hydrogen production via a two-step
609 splitting thermochemical cycle based on metal oxide-A review, Applied Energy, 267, 114860, 2020
- 610 [9] Carrillo R, Scheffe J. Advances and trends in redox materials for solar thermochemical fuel
611 production, Solar Energy, 156, pp.3-20, 2017
- 612 [10] Bulfin B, Vieten J, Agrafiotis C, Roeb M, Sattler C. Applications and limitations of two-step metal
613 oxide thermochemical redox cycles; A review, Journal of Materials Chemistry A, 5, 18951-18966,
614 2017
- 615 [11] Wim H, Geerlings H. Efficient production of solar fuel using existing large scale production
616 technologies, Environmental science technology, 45, pp.8609-8610, 2011
- 617 [12] Kim J, Johnson T, Miller J, Stetchel E, Maravelias C. Fuel production from CO₂ using solar-thermal
618 energy: system level analysis, Energy and environmental science, 5, pp.8417-8429, 2012

- 619 [13]Schappi R, Rutz D, Dahler F, Muroyama A, Haueter P, Lilliestam J, Patt A, Furler P, Steinfeld A. Drop-
620 in fuels from sunlight and air, *Nature*, 601, pp.63-68, 2022
- 621 [14]Zoller S, Koepf E, Nizamian D, Stephan M, Patane A, Haueter P, Romero M, Gonzales-Aguilar J,
622 Lieftink D, de Wit E, Brendelberger S, Sizmann A, Steinfeld A. A solar tower fuel plant for the
623 thermochemical production of kerosene from H₂O and CO₂, *Joule*, 6, pp.1606-1616, 2022
- 624 [15]Welte M, Barhoumi R, Zbinden A, Scheffe J, Steinfeld A. Experimental demonstration of the
625 thermochemical reduction of ceria in a solar aerosol reactor. *Ind Eng Chem Res*, 55, 10618–25,
626 2016
- 627 [16]Ermanoski I, Siegel N, Stechel E. A new reactor concept for efficient solar-thermochemical fuel
628 production. *J Sol Energy Eng*, 135, 031002, 2013
- 629 [17]Kaneko H, Miura T, Fuse A, Ishihara H, Taku S, Fukuzumi H, et al. Rotary-type solar reactor for solar
630 hydrogen production with two-step water splitting process. *Energy Fuels*, 21, 2287–93, 2007
- 631 [18]Lapp J, Davidson J, Lipinski W. Heat transfer analysis of a solid-solid heat recuperation system for
632 solar-driven nonstoichiometric redox cycles. *J Sol Energy Eng*, 135, 031004, 2013
- 633 [19]Agrafiotis C, Roeb M, Konstandopoulos A, Nalbandian L, Zaspalis V, Sattler C, et al. Solar water
634 splitting for hydrogen production with monolithic reactors. *Sol Energy*, 79, 409–21, 2005
- 635 [20]Chueh W, Falter C, Abbott M, Scipio D, Furler P, Haile S, et al. High-flux solar-driven thermochemical
636 dissociation of CO₂ and H₂O using nonstoichiometric ceria. *Science*, 330, 1797–801, 2010
- 637 [21]Marxer D, Furler P, Takacs M, Steinfeld A. Solar thermochemical splitting of CO₂ into separate
638 streams of CO and O₂ with high selectivity, stability, conversion, and efficiency. *Energy Environ Sci*,
639 10, 1142–9, 2017
- 640 [22]Zhu L, Lu Y, Shen S. Solar fuel production at high temperatures using ceria as a dense membrane.
641 *Energy*, 104, 53–63, 2016.
- 642 [23] Lou J, Tian Z, Wu Y, Li X, Qian X, Haile S, Hao Y. Thermodynamic assessment of nonstoichiometric
643 oxides for solar thermochemical fuel production, *Solar Energy*, 241, pp.504-514, 2022

- 644 [24]Yang C, Yamazaki Y, Aydin A, Haile S. Thermodynamic and kinetic assessment of strontium-doped
645 lanthanum manganite perovskites for two-step thermochemical water splitting, *J. Mater. Chem.*,
646 2, pp.13612-13623, 2014
- 647 [25]Kim Y, Jeong S, Koo B, Lee S, Kwak N, Jung W. Study of the surface reaction kinetics of (La,Sr)MnO₃
648 oxygen carriers for solar thermochemical fuel production, *J. Mater. Chem.*, 6, p.13082-13089, 2018
- 649 [26]Lu Y, Zhu L, Agrafiotis C, Vieten J, Roeb M, Sattler C. Solar fuel production: two-step
650 thermochemical cycles with cerium-based oxides, *Progress in energy and combustion science*, 75,
651 pp.100785, 2019
- 652 [27]Marxer D, Furler P, Takacs M, Steinfeld A. Solar thermochemical splitting of CO₂ into separate
653 streams of CO and O₂ with high selectivity, stability, conversion, and efficiency, *Energy Environ Sci.*,
654 10, pp.1142–1149, 2017
- 655 [28]Kubicek M, Bork A, Rupp J. Perovskite oxides – a review on a versatile material class for solar-to-
656 fuel conversion process, *Journal of materials chemistry A*, 5, 11983-12000, 2017
- 657 [29]Bayon A, de la Calle A, Kamol Ghose K, Page A, McNaughton R. Experimental, computational and
658 thermodynamic studies in perovskites metal oxides for thermochemical fuel production: A review,
659 *International journal of hydrogen energy*, 45, 12653-12679, 2020
- 660 [30]Haeussler A, Abanades S, Jouannaux J, Julbe A. Non-stoichiometric redox active perovskite
661 materials for solar thermochemical fuel production: A review, *Catalysts*, 8, 611, 2018
- 662 [31]Zhai S, Rojas J, Ahlborg N, Lim K, Toney M, Jin H, Chueh W. Majumdar A. The use of poly-cation
663 oxides to lower the temperature of two-step thermochemical water splitting, *Energy and
664 environmental science*, 11, 2172-2178, 2018
- 665 [32]Gao Y, Mao Y, Song Z, Zhao X, Sun J, Wang W, Chen G, Chen S. Efficient generation of hydrogen by
666 two-step thermochemical cycles: Successive thermal reduction and water splitting reactions using
667 equal-power microwave irradiation and a high entropy material, *Applied Energy*, 279, 115777,
668 2020

669 [33]Gao Y, Zhang M, Mao Y, Cao H, Zhang S, Wang W, Sun C, Song Z, Sun J, Zhao X. Microwave-triggered
670 low temperature thermal reduction of Zr-modified high entropy oxides with extraordinary
671 thermochemical H₂ production performance, *Energy conversion and management*, 252, 115125,
672 2022

673 [34]Luo J. New high entropy perovskite oxides with increased reducibility and stability for
674 thermochemical hydrogen generation, US DOE project review, 2020,
675 https://www.hydrogen.energy.gov/pdfs/review20/p194_luo_2020_p.pdf,

676 [35] Le Gal A, Valles M, Julbe A, Abanades S. Thermochemical properties of high entropy oxides used
677 as redox-active materials in two-step solar fuel production cycles, *Catalysts*, 12, pp.1116, 2022

678 [36]Haeussler A, Abanades S, Julbe A, Jouannaux J., Cartoixa B., Solar thermochemical fuel production
679 from H₂O and CO₂ splitting via two-step redox cycling of reticulated porous ceria structures
680 integrated in a monolithic cavity-type reactor, *Energy*, 201, 117649, 2020

681 [37]Orfila M, Sanz D, Linares M, Molina R, Sanz R, Marugan J, Botas J. H₂ production by thermochemical
682 water splitting with reticulated porous structures of ceria-based mixed oxide materials,
683 *International journal of hydrogen energy*, 46, 17458-17471, 2021

684 [38]Cho H, Kodama T, Gokon N, Bellan S, Kim J. Development of synthesis and fabrication process for
685 Mn-CeO₂ foam via two-step water splitting cycle hydrogen production, *Energies*, 14, 6919, 2021

686 [39]Hoes M, Ackermann S, Theiler D, Furler P, Steinfeld A. Additive-manufactured ordered porous
687 structures made of ceria for concentrated solar applications, *Energy technology*, 7, 1900484, 2019

688 [40]Haeussler A, Abanades S. Additive manufacturing and two-step redox cycling of ordered porous
689 ceria structures for solar driven thermochemical fuel production, *Chemical engineering science*,
690 246, 116999, 2021

691 [41]Furler P, Scheffe J, Marxer D, Gorbar M, Bonk A, Vogt U, Steinfeld A. Thermochemical CO₂ splitting
692 via redox cycling of ceria reticulated foam structures with dual-scale porosities, *Phys. Chem. Chem.*
693 *Phys.*, 16, pp.10503-10511, 2014

694 [42]Pullar R, Novais R, Caetano A, Barreiros M, Abanades S, Costa Oliveira F. A review of solar
695 thermochemical CO₂ splitting using ceria-based ceramics with designed morphologies and
696 microstructures, *Frontiers in chemistry*, 7, 601,2019

697 [43]Abanades S, Haeussler A. Two-step thermochemical cycles using fibrous ceria pellets for H₂
698 production and CO₂ reduction in packed-bed solar reactor, *Sustainable materials and technologies*,
699 29, e00328, 2021

700 [44]Haeussler A, Abanades S, Costa Oliveira F A, Novais R, Pullar R. Solar redox cycling of ceria
701 structures based on fiber boards, foams and biomimetic cork-derived ecoceramics for two-step
702 thermochemical H₂O and CO₂ splitting, *Energy and fuels*, 34, pp.9037-9049, 2020

703 [45]Furler P, Scheffe J, Steinfeld A. Syngas production by simultaneous splitting of H₂O and CO₂ via
704 ceria redox reactions in a high temperature solar reactor. *Energy & environmental science*. 3,
705 pp.6098-6103, 2012

706 [46]Haeussler A, Abanades S, Julbe A, Ayrál A, Cartoixa B. Remarkable performance of microstructured
707 ceria foams for thermochemical splitting of H₂O and CO₂ in a novel high-temperature solar reactor,
708 *Chemical Engineering Research and Design*, 156, pp.311-323, 2020

709 [47]Abanades S, Haeussler A, Julbe A. Synthesis and thermochemical redox cycling of porous ceria
710 microspheres for renewable fuels production from solar-aided water-splitting and CO₂ utilization,
711 *Applied physics letters*, 119 (2), 023902, 2021

712 [48]Costa Oliveira F, Barreiros M, Haeussler A, Caetano A, Mouquinho P, Oliveira Silva R, Novais
713 A, Pullar R, Abanades S. High performance cork-templated ceria for solar thermochemical
714 hydrogen production via two-step water-splitting cycles, *Sustainable Energy and Fuels*, 4(6), pp.
715 3077–3089, 2020

716 [49]Costa Oliveira F, Barreiros M, Abanades S, Caetano A, Novais R, Pullar R. Solar thermochemical
717 CO₂ splitting using cork-templated ceria ecoceramics, *Journal of CO₂ Utilization*, 26, pp. 552–563,
718 2018

719 [50]Haeussler A, Abanades S, Jouannaux J, Drobek M, Ayrat A, Julbe A. Recent progress on ceria doping
720 and shaping strategies for solar thermochemical water and CO₂ splitting cycles, AIMS Materials
721 Science, 6(5), pp. 657–684, 2019

722 [51]Haeussler A, Abanades S, Julbe A, Jouannaux J, Cartoixa B. Two-step CO₂ and H₂O splitting using
723 perovskite-coated ceria foam for enhanced green fuel production in a porous volumetric solar
724 reactor, Journal of CO₂ Utilization, 41, 101257, 2020

725 [52]Schwartzwalder K, Somers H, Somers V. Method of making porous ceramic articles, U.S.P office,
726 1963

727