Doctoral Thesis

A 50 kW Solar Thermochemical Reactor for Syngas Production Utilizing Porous Ceria Structures

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A 50 kW SOLAR THERMOCHEMICAL REACTOR FOR SYNGAS PRODUCTION UTILIZING POROUS CERIA STRUCTURES

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by

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Abstract

This thesis reports on the development, optimization and experimental testing of a solar receiver-reactor for the thermochemical splitting of H$_2$O and CO$_2$ to produce H$_2$ and CO (syngas). The solar reactor allows to apply a temperature and pressure swing redox cycle to pure ceria in the form of a reticulated porous ceramic (RPC). In the first, endothermic step, the ceria RPC is directly heated with concentrated solar radiation to around 1500 °C while under vacuum pressure of less than 100 mbar, thereby releasing oxygen from its crystal lattice. In the subsequent, exothermic step, the reactor is repressurized with H$_2$O and/or CO$_2$ as it cools, and at temperatures typically below 1000 °C, the partially reduced ceria is re-oxidized with a flow of H$_2$O and/or CO$_2$ at atmospheric pressure. The produced syngas can be catalytically processed to conventional liquid hydrocarbon fuels.

A reactor prototype at the 4 kW scale has been previously designed and tested using a high-flux solar simulator. In this work, the same reactor technology is realized and optimized at the 50 kW scale and tested under realistic conditions using a solar concentrating facility located in Móstoles, Spain.

Initial experiments focused on comparing the cycling performance and the mechanical stability of three different ceria cavities made of an interlocking structure of RPC bricks with different porosities, thicknesses and geometries. The performance of the solar reactor for CO$_2$ splitting was experimentally assessed in a high-flux solar simulator. The mechanical strength and stability of the RPCs was assessed with three-point bend testing after fabrication and visually after testing in the solar reactor. The results indicate that lower porosity and higher thickness, both resulting in a higher ceria mass loading, are generally beneficial for the mechanical integrity of the RPC cavity, but the addition of mass without ensuring effective volumetric absorption of the solar radiation and
uniform heating of the ceria does not increase the reactor performance. The maximum power of the solar simulator was limited to 32.2 kW delivered at the 16 cm diameter aperture of the solar reactor, which corresponds to a solar concentration ratio of 1602 suns. As a result of the limited power input, a relatively low maximum solar-to-fuel conversion efficiency, defined as the ratio of the heating value of the fuel produced to the input of solar radiative energy and the energy penalties associated with inert gas separation and vacuum pumping, of 3.48±0.08% was measured. Stable operation over multiple cycles without observable degradation was shown with an extended experiment of five consecutive CO\textsubscript{2} splitting cycles.

To further analyse the performance of the solar reactor and to gain insight into improved design and operation conditions, a transient heat transfer model of the solar reactor was developed. The numerical model couples the incoming concentrated solar radiation using Monte Carlo ray tracing, incorporates the reduction chemistry by assuming thermodynamic equilibrium, and accounts for internal radiation heat transfer inside the porous ceria by applying effective heat transfer properties. The model was experimentally validated using the data acquired in the high-flux solar simulator. The numerical results highlight the potential of the solar reactor to reach high solar-to-fuel energy conversion efficiencies when operated at high power levels. At a solar radiative power input of 50 kW, an efficiency exceeding 6% is predicted. If the RPC macroporosity could be substantially increased to achieve better volumetric absorption of radiation and uniform heating of the ceria, the model predicts efficiencies exceeding 10%.

Based on the experimental results acquired in the high-flux solar simulator and the numerical results of the heat transfer model, a new ceria RPC cavity was designed for the operation of the solar reactor with the solar concentrating facility located in Móstoles, Spain. The facility consists of 169 heliostats which concentrate sunlight onto a tower with an optical height of 15 m. The solar reactor, situated on top of the tower, is facing downwards onto the heliostats and features a self-supporting design of the ceria RPC cavity that is adapted for the inclination angle of 40 degrees. With this adjusted solar reactor, a maximum
solar-to-fuel energy conversion efficiency of 5.6±1.0% is experimentally
demonstrated for CO₂ splitting at a solar radiative power input of 55.8±8.2 kW. Simulating the same experiment using the transient heat transfer model reveals how the performance of the reactor could be further improved. At a power input of 55.8 kW, 21.0% of the total solar energy input is lost by reradiation from the hot cavity, but by far the biggest share of energy is used for sensible heating of the ceria and the bulk reactor components, accounting for 58.4% of the solar energy input in total. This energy is mostly lost when the reactor cools down to the oxidation temperature, which highlights the need for implementing heat recovery in order to increase the efficiency of such reactor technology in the future.

For the co-splitting of H₂O and CO₂ in the solar reactor, different measures to adjust the composition of the produced syngas are discussed. At optimal operating conditions, 62 consecutive redox cycles are performed with the same ceria RPC cavity. The produced syngas is collected and stored in a pressurized gas cylinder. Within the European research consortium SUN-to-LIQUID, the accumulated syngas is further processed via Fischer-Tropsch synthesis to produce liquid hydrocarbon fuels on-site.

This work demonstrates the technical feasibility of solar thermochemical H₂O and CO₂ splitting via ceria redox cycling under real-world conditions and at a relevant scale and as such contributes towards the development of a commercial application for the production of solar hydrocarbon fuels.
Zusammenfassung


Ein 4 kW Reaktorprototyp wurde im Vorfeld dieser Arbeit entwickelt und mithilfe eines Hochfluss-Sonnensimulators getestet. In dieser Arbeit wird dieselbe Reaktortecnologie für eine Betriebsgrösse von 50 kW umgesetzt und optimiert sowie unter realistischen Betriebsbedingungen mithilfe einer Anlage zur Konzentration von Sonnenlicht in Móstoles, Spanien, getestet.


Wirkungsgrad größer als 6% vorausgesagt. Falls die Makroporosität der RPC Struktur erheblich erhöht werden könnte um eine volumetrische Absorption der eingehenden Strahlung und ein gleichmässigeres Aufheizen des Cerdioxids zu erreichen, so könnten gemäss Modell Wirkungsgrade erreicht werden die 10% übersteigen.


Für das gleichzeitige Spalten von H₂O und CO₂ im Solarreaktor werden verschiedene Möglichkeiten aufgezeigt um die Zusammensetzung des produzierten Synthesegases zu regulieren. Unter optimalen Betriebsbedingungen werden ausserdem 62 aufeinanderfolgende Redox-Zyklen mit derselben Kavität aus Cerdioxid RPCs durchgeführt. Das produzierte Synthesegas wird gesammelt
und in einem Druckbehälter gelagert. Das gesammelte Synthesegas wird im Rahmen des europäischen Forschungsprojekts SUN-to-LIQUID mittels Fischer-Tropsch Synthese vor Ort zu flüssigen Kohlenwasserstoff-Treibstoffen weiterverarbeitet.

Diese Arbeit demonstriert die technische Umsetzbarkeit der solaren thermochemischen Spaltung von H₂O und CO₂ mittels Redox-Zyklen basierend auf Cerdioxid unter realistischen Betriebsbedingungen und in einer relevanten Größenordnung. Als solches trägt die Arbeit zu der Entwicklung einer kommerziellen Anwendung für die Produktion von solaren Kohlenwasserstoff-Treibstoffen bei.
Acknowledgements

I am thankful to a great number of people who contributed to the successful completion of this work. Without them, this would certainly not have been possible.

First, I want to thank Prof. Dr. Aldo Steinfeld for giving me the unique opportunity to conduct my doctoral thesis under his supervision at the Professorship of Renewable Energy Carriers (PREC) at ETH Zurich. I am thankful for his confidence in my work, the autonomy granted especially while not working at ETH Zurich, and the exciting opportunity to conduct a large part of my thesis in Spain.

I thank Prof. Dr. Martin Kaltschmitt from the Technical University of Hamburg for acting as co-examiner of my thesis.

My very special thanks go to Dr. Erik Koepf who directly supervised my work during the first two years and kept on offering his advice when needed even while he did not work for ETH Zurich anymore. I thank him for his guidance and support especially in tougher times, for countless fruitful discussions, and for his friendship.

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Nomenclature

Latin characters

\( A_{fs} \) fluid-solid area density \( \text{m}^{-1} \)
\( C \) solar concentration ratio \( \text{suns} \)
\( c_p \) heat capacity \( \text{J mol}^{-1} \text{K}^{-1} \)
\( d_m \) mean pore diameter \( \text{m} \)
\( E_{\text{inert}} \) energy required for inert gas separation \( \text{J mol}^{-1} \)
\( h \) enthalpy \( \text{J} \)
\( h_{fs} \) interfacial heat transfer coefficient \( \text{W m}^{-2} \text{K}^{-1} \)
\( \Delta H_{\text{CO}} \) higher heating value of CO \( \text{J mol}^{-1} \)
\( \Delta H_{\text{fuel}} \) higher heating value of the fuel \( \text{J mol}^{-1} \)
\( \Delta H_{O_2} \) reaction enthalpy \( \text{kJ mol}^{-1} \)
\( \Delta H_{H_2} \) higher heating value of \( \text{H}_2 \) \( \text{J mol}^{-1} \)
\( I \) radiation intensity \( \text{W m}^{-2} \)
\( I_b \) blackbody radiation emission intensity \( \text{W m}^{-2} \)
\( k \) thermal conductivity \( \text{W m}^{-1} \text{K}^{-1} \)
\( k_{\text{eff}} \) effective thermal conductivity of ceria RPC \( \text{W m}^{-1} \text{K}^{-1} \)
\( M \) molar mass \( \text{kg mol}^{-1} \)
\( m_{\text{RPC}} \) ceria RPC cavity mass loading \( \text{kg} \)
\( \dot{n} \) molar gas flow rate \( \text{mol s}^{-1} \)
\( n_{\text{fuel}} \) amount of fuel produced \( \text{mol} \)
\( \dot{n}_{\text{H}_2\text{O}} \) molar flow rate of \( \text{H}_2\text{O} \) during oxidation \( \text{mol s}^{-1} \)
\( n_{\text{ppi}} \) number of pores per inch
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{solar}}$</td>
<td>solar radiative power input</td>
<td>kW</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_{\text{atm}}$</td>
<td>atmospheric pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>oxygen partial pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_{\text{reactor}}$</td>
<td>reactor pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_{\text{red}}$</td>
<td>Reactor pressure at end of reduction</td>
<td>Pa</td>
</tr>
<tr>
<td>$Q_{\text{aux}}$</td>
<td>auxiliary energy needed in the process</td>
<td>J</td>
</tr>
<tr>
<td>$Q_{fs}$</td>
<td>fluid-solid heat source</td>
<td>W</td>
</tr>
<tr>
<td>$Q_{\text{fuel}}$</td>
<td>integrated heating value of the fuel produced</td>
<td>J</td>
</tr>
<tr>
<td>$Q_{\text{inert}}$</td>
<td>heat equivalent of work for inert gas separation</td>
<td>J</td>
</tr>
<tr>
<td>$Q_{\text{pump}}$</td>
<td>heat equivalent of work for vacuum pumping</td>
<td>J</td>
</tr>
<tr>
<td>$Q_{sf}$</td>
<td>solid-fluid heat source</td>
<td>W</td>
</tr>
<tr>
<td>$Q_{\text{solar}}$</td>
<td>solar radiative energy input</td>
<td>J</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
<td>J K$^{-1}$ mol$^{-1}$</td>
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<tr>
<td>$r$</td>
<td>total hemispherical reflectance of ceria</td>
<td></td>
</tr>
<tr>
<td>$\bar{r}$</td>
<td>position vector</td>
<td></td>
</tr>
<tr>
<td>$r_{CO}$</td>
<td>molar rate of CO produced</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$r_{\text{fuel}}$</td>
<td>molar rate of fuel produced</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$r_{H_2}$</td>
<td>molar rate of H$_2$ produced</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$r_{\text{inert}}$</td>
<td>molar rate of inert gas Ar consumed</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$r_{O_2}$</td>
<td>molar rate of O$_2$ released</td>
<td>mol s$^{-1}$</td>
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<tr>
<td>$s$</td>
<td>path length</td>
<td>m</td>
</tr>
<tr>
<td>$\bar{s}$</td>
<td>direction vector</td>
<td></td>
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<tr>
<td>$S_{\text{radiation}}$</td>
<td>radiation exchange source</td>
<td>W m$^{-3}$</td>
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<tr>
<td>$S_{\text{reaction}}$</td>
<td>reaction energy source</td>
<td>W m$^{-3}$</td>
</tr>
<tr>
<td>$S_{\text{solar}}$</td>
<td>absorbed solar radiation source</td>
<td>W m$^{-2}$/W m$^{-3}$</td>
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### Nomenclature

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_f$</td>
<td>fluid temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_{ox,\text{end}}$</td>
<td>oxidation end temperature</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{ox,\text{start}}$</td>
<td>oxidation start temperature</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{\text{pump}}$</td>
<td>vacuum pump temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_{\text{red,\text{end}}}$</td>
<td>end temperature of reduction step</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{\text{red,\text{start}}}$</td>
<td>start temperature of reduction step</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{\text{RPC,\text{max}}}$</td>
<td>maximum temperature of RPC</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{\text{RPC,\text{nom}}}$</td>
<td>nominal temperature of RPC (measured at back surface)</td>
<td>°C</td>
</tr>
<tr>
<td>$T_s$</td>
<td>solid temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$t_{\text{ox}}$</td>
<td>duration of the oxidation step</td>
<td>min</td>
</tr>
<tr>
<td>$t_{\text{red}}$</td>
<td>duration of the reduction step</td>
<td>min</td>
</tr>
<tr>
<td>$t_{\text{RPC}}$</td>
<td>RPC thickness</td>
<td>mm</td>
</tr>
<tr>
<td>$\dot{V}_{\text{Ar}}$</td>
<td>volumetric flow rate of Ar during reduction</td>
<td>L min$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>(at 273.15 K and 101’325 Pa)</td>
<td></td>
</tr>
<tr>
<td>$\dot{V}_{\text{CO}_2}$</td>
<td>volumetric flow rate of CO$_2$ during oxidation</td>
<td>L min$^{-1}$</td>
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<tr>
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<td>(at 273.15 K and 101’325 Pa)</td>
<td></td>
</tr>
<tr>
<td>$\dot{V}_{\text{H}_2\text{O}}$</td>
<td>volumetric flow rate of H$_2$O during oxidation</td>
<td>L min$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>(at 373.15 K and 101’325 Pa)</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>depth within RPC</td>
<td>mm</td>
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### Greek characters

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<th>Symbol</th>
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<tr>
<td>$\alpha$</td>
<td>absorption coefficient</td>
<td>m$^{-1}$</td>
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<tr>
<td>$\beta$</td>
<td>extinction coefficient</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>nonstoichiometry of ceria</td>
<td></td>
</tr>
</tbody>
</table>
Nomenclature

\( \varepsilon \)  
**total hemispherical emittance**

\( \eta_{\text{heat-to-work}} \)  
**heat-to-work energy conversion efficiency**

\( \eta_{\text{pump}} \)  
**vacuum pumping efficiency**

\( \eta_{\text{solar-to-fuel}} \)  
**solar-to-fuel energy conversion efficiency**

\( \rho \)  
**density**  
\( \text{kg m}^{-3} \)

\( \sigma \)  
**scattering coefficient**  
\( \text{m}^{-1} \)

\( \tau \)  
**transmissivity of quartz window**

\( \tau_{\text{RPC}} \)  
**optical thickness of ceria RPC**

\( \phi_{\text{dual}} \)  
**dual-scale porosity of ceria RPC**

\( \phi_{\text{single}} \)  
**single-scale porosity of ceria RPC**

\( \phi_{\text{strut}} \)  
**strut porosity of ceria RPC**

\( \omega \)  
**solid angle**  
\( \text{deg} \)

Subscripts

\( \text{Al} \)  
**aluminum front**

\( \text{B,1–B,3} \)  
**type-B thermocouple positions**

\( \text{ins} \)  
**Al\text{\textsubscript{2}}O\text{\textsubscript{3}}–SiO\text{\textsubscript{2}} insulation**

\( \text{jacket} \)  
**insulating jacket**

\( \text{K,1–K,5} \)  
**type-K thermocouple positions**

\( \text{ox} \)  
**oxidation**

\( \text{red} \)  
**reduction**

\( \text{shell} \)  
**stainless steel 316 shell**

\( \infty \)  
**ambient conditions**
**Abbreviations**

- **CAD**: computer-aided design
- **CCD**: charge-coupled device
- **CPC**: compound parabolic concentrator
- **CSP**: concentrated solar power
- **DNI**: direct normal irradiance
- **ETH**: Swiss Federal Institute of Technology
- **FMAS**: flux measurement acquisition system
- **HFSS**: high-flux solar simulator
- **IR**: infrared
- **MC**: Monte Carlo
- **ppi**: pores per inch
- **PSI**: Paul Scherrer Institute
- **PU**: polyurethane
- **RPC**: reticulated porous ceramic
- **SLPM**: standard liters per minute at 273.15 K and 101.325 Pa
1 Introduction

In 2017, the world’s primary energy demand was around 13’972 Mtoe\(^1\), out of which 81% was covered by fossil fuels (26.8% coal, 31.7% oil, 22.2% gas) [1]. By 2040, driven by population growth, urbanization and economic growth, the demand is expected to grow to 13’715–19’328 Mtoe, depending on the scenario chosen for calculation [1]. Meanwhile, due to the extensive use of fossil fuels over the last decades, the atmospheric concentration of CO\(_2\) increased from the preindustrial level in the range of 275–285 ppm [2] to 405.0±0.1 ppm in 2017 [3]. In order to limit corresponding global warming, the total cumulative global anthropogenic emissions of CO\(_2\) since the preindustrial period need to be limited, or in other words, stay within a total carbon budget. The remaining carbon budget to limit global warming to 1.5 °C is estimated to be in the range of 420–770 Gt CO\(_2\) with substantial uncertainties, while current emissions are at 42±3 Gt CO\(_2\) per year [4].

Regarding electricity production, many commercial technologies already exist that use renewable energy sources such as hydropower, wind, and solar. Some technologies though are hard to electrify, and especially for the aviation sector, analyses show that for many years to come, long-range travel is very likely to rely on hydrocarbon fuels because of the limited energy density of batteries [5]. For these industries, synthetic hydrocarbon fuels might be an ideal solution. They offer the added benefit of a drop-in technology, meaning that they are compatible with our existing transportation infrastructure.

Synthetic hydrocarbon fuels can either be produced from biomass, or directly from H\(_2\)O and CO\(_2\) [6]. Following the latter approach, H\(_2\)O and CO\(_2\) are first split into H\(_2\) and CO, a mixture called synthesis gas or syngas. A range of technologies

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\(^1\) 1 Mtoe (million tonnes of oil equivalent) = 11.63 TWh = 41.868 PJ
exist for the highly endothermic dissociation of H₂O and/or CO₂, such as photocatalysis [7-9], electrolysis [10, 11], and thermochemical processes [12, 13]. The syngas is then converted into liquid hydrocarbon fuels such as synthetic kerosene, diesel, gasoline, or methanol via industrially implemented catalytic processes, such as the Fischer-Tropsch process [14, 15]. If the CO₂ needed for the production of the syngas is filtered from ambient air, the carbon loop is closed, as the same amount of CO₂ that is released when burning the fuel is needed for its production, and net CO₂ emissions result only from the construction and operation of the fuel production facility [16]. First commercial technologies for capturing CO₂ from ambient air are available today [17, 18]. The concept of a closed carbon cycle with all the involved process steps is schematically shown in Figure 1.1 for the case of solar thermochemical H₂O and CO₂ splitting.

**Figure 1.1.** Process scheme for the production of liquid hydrocarbon fuels from concentrated sunlight, water and carbon dioxide. H₂O and CO₂ are captured and stored, and split in a solar thermochemical process, driven by concentrated sunlight, into H₂ and CO, which is stored and further processed via Fischer-Tropsch to liquid hydrocarbon fuels. The amount of CO₂ released when burning these fuels corresponds to the amount of CO₂ needed for the fuel production.
1.1 Solar thermochemical H\textsubscript{2}O and CO\textsubscript{2} splitting

Using concentrated solar radiation to drive the dissociation of H\textsubscript{2}O and CO\textsubscript{2} is of special interest because of the vast abundance of solar energy. The solar radiative power striking the earth’s surface is around 94 PW [19], meaning that in less than two hours, the world’s primary energy demand of the year 2017 (162 PWh [1]) arrives at the earth’s surface by means of solar energy. H\textsubscript{2}O and CO\textsubscript{2} can be thermally decomposed directly, but this requires very high temperatures [20, 21]. For H\textsubscript{2}O splitting for example, temperatures well above 2000 K are required to obtain significant concentrations of H\textsubscript{2} [22]. In addition, the high temperature separation of the gaseous products or the rapid quenching of the gas mixture in order to avoid recombination is technically very challenging [23].

Two-step solar thermochemical splitting of H\textsubscript{2}O and CO\textsubscript{2} offers the advantage that the fuel (H\textsubscript{2} and/or CO) and oxygen are released in separate steps, apart from typically lower temperatures compared to direct thermal decomposition. The two-step solar thermochemical cycle using metal oxides is schematically shown in Figure 1.2. In the first, endothermic reduction step, a generic metal oxide is reduced from the oxidized state (MO\textsubscript{ox}) to the reduced state (MO\textsubscript{red}) using concentrated solar radiation to provide the reaction enthalpy. The reduction is thermodynamically favored at high temperatures and low oxygen partial pressure (p\textsubscript{O\textsubscript{2}}). While high temperatures can be reached using concentrated solar radiation, low p\textsubscript{O\textsubscript{2}} is typically reached using an inert gas to sweep the released O\textsubscript{2}, by lowering the total pressure, or a combination of both. In the second, exothermic oxidation step, the reduced metal oxide is re-oxidized back to the initial state with H\textsubscript{2}O and/or CO\textsubscript{2} to produce H\textsubscript{2} and/or CO. This step is thermodynamically favored at lower temperatures, and no heat input is needed because the reaction is exothermic. The metal oxide is then recycled back to the reduction step. Because the metal oxide is not consumed in the process, the net reactions are

\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad (1.1) \\
\text{CO}_2 & \rightarrow \text{CO} + \frac{1}{2}\text{O}_2 \quad (1.2)
\end{align*}

with concentrated solar energy used to provide the process heat.
Figure 1.2. Schematic of the two-step solar thermochemical H₂O and CO₂ splitting cycle using metal oxides. In the first, endothermic step, the metal oxide is reduced from the oxidized state (MO₉x) to the reduced state (MO₉red) using concentrated solar radiation to provide the process heat, thereby releasing oxygen. In the second, exothermic step, the reduced metal oxide is re-oxidized with H₂O and/or CO₂ to its initial state, thereby producing H₂ and/or CO. The metal oxide is then recycled to the reduction step.

The performance of a solar thermochemical cycle is typically reported in terms of the solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$, defined as

$$\eta_{\text{solar-to-fuel}} = \frac{\Delta H_{\text{fuel}} \cdot n_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{aux}}}$$  \hspace{1cm} (1.3)$$

where $\Delta H_{\text{fuel}}$ is the higher heating value of the fuel, $n_{\text{fuel}}$ is the amount of fuel produced, $Q_{\text{solar}}$ is the solar energy input and $Q_{\text{aux}}$ summarizes all auxiliary energy needed in the process, for example for inert gas separation or vacuum pumping. The efficiency $\eta_{\text{solar-to-fuel}}$ is a key indicator for solar thermochemical processes that allows comparing the performance of different technologies.

Several metal oxides have been proposed as reactive intermediates for two-step solar thermochemical splitting of H₂O and CO₂ [24-27], such as iron oxide [28-31], ferrites [32-34], zinc oxide [35-40], perovskites [41-46], ceria [47-53], and doped ceria [54-58]. These metal oxides can be categorized as volatile and non-
volatile materials. Volatile metal oxides change from the solid to the gaseous phase during reduction, while non-volatile materials remain in the solid state.

An example for a volatile cycle is the ZnO/Zn cycle. Solid ZnO thermally dissociates to gaseous Zn and O$_2$ at temperatures around 2000 K. To avoid the recombination of the gaseous mixture of Zn and O$_2$, high temperature gas separation or rapid quenching to ambient temperature is needed, which is technically challenging and implies a significant energy penalty for the process. Once at ambient temperature, the solid Zn can be stored, and the reduction and oxidation steps can be decoupled in space and in time. ZnO and volatile metal oxides in general typically offer larger oxygen exchange capacities compared to non-volatile metal oxides, meaning that they release more oxygen and as a result can produce more fuel per mass of metal oxide. Therefore, theoretical efficiencies of up to 39% are estimated for CO$_2$ splitting via the ZnO/Zn cycle when the solar reactor is operated at 2000 K [59]. The experimental implementation though was shown to be very challenging, especially at a relevant scale. For example, with a 100 kW reactor tested in a solar furnace, a maximum solar-to-fuel efficiency of 0.17% was measured, primarily because of low Zn yields associated with the challenging quenching of product gases [60].

Non-volatile metal oxides can be categorized as materials that react stoichiometrically and materials that release only a fraction of the oxygen contained in the lattice, thereby being reduced to a nonstoichiometric state. An example for a non-volatile, stoichiometric redox cycle is the Fe$_3$O$_4$/FeO cycle, which was the first two-step thermochemical cycle proposed for hydrogen production in 1977 [31]. For the thermal decomposition of magnetite (Fe$_3$O$_4$) to iron oxide (FeO), temperatures of up to 2500 K are necessary, which hinders the technical implementation of the process. The reduction temperature can be lowered by introducing small amounts of other metals such as Co, Ni, Zn or Mn into the iron oxide, a process called doping, to form mixed-metal ferrites, and stabilizing the material with inert supports such as zirconia or yttria-stabilized zirconia [33]. This approach is followed for example within the Hydrosol project, which aims to build a hydrogen production plant with a thermal power input of 750 kW that consists of three identical solar reactors with directly irradiated,
porous monoliths of pure nickel-ferrite, developed by the German Aerospace Center (DLR) [61]. Remaining problems with ferrites are sintering and side reactions with supporting materials that can lead to a rapid degradation of active material over time [29, 62].

Examples for nonstoichiometric, non-volatile metal oxides are doped and undoped ceria and perovskites. A generic representation of perovskites is ABO$_3$, where A and B denote metal cations that can be doped with many different materials [45]. Some perovskites show relatively high reduction extents at moderate temperature, but good reduction characteristics usually come at the expense of unfavorable oxidation characteristics, such as low oxidation temperatures or the need for a large excess of the oxidant gas [46]. However, due to the huge number of possible perovskites, the screening of potential candidates and testing for cycling performance and stability is ongoing research.

1.2 The ceria cycle

Ceria, or cerium dioxide (CeO$_2$), has emerged as an attractive redox material and is currently considered the state-of-the-art material for solar thermochemical H$_2$O and CO$_2$ splitting. It offers a relatively large oxygen exchange capacity (i.e. high nonstoichiometry) for a non-volatile, nonstoichiometric metal oxide [63-65], rapid redox kinetics [66-68] and is morphologically stable over a large range of temperatures and reduction extents [48, 69]. Cerium is the most abundant and least expensive rare earth metal with similar concentration in the earth’s crust to commonplace industrial metals such as nickel or copper [70]. The two-step thermochemical cycle using ceria as reactive intermediate is represented by, first, an endothermic reduction

$$\text{CeO}_2 \rightarrow \text{CeO}_{2-\delta} + \frac{\delta}{2}\text{O}_2$$

(1.4)

And, second, an exothermic oxidation with H$_2$O and/or CO$_2$

$$\text{CeO}_{2-\delta} + \delta\text{H}_2\text{O} \rightarrow \text{CeO}_2 + \delta\text{H}_2$$

(1.5)

$$\text{CeO}_{2-\delta} + \delta\text{CO}_2 \rightarrow \text{CeO}_2 + \delta\text{CO}$$

(1.6)
where $\delta$ denotes the nonstoichiometry, which is a measure of the amount of oxygen exchanged during reduction and oxidation. In the first, solar reduction step, ceria is typically reduced at low oxygen partial pressures and elevated temperatures of around 1500 °C, where the process heat is delivered by concentrated solar energy. In the second oxidation step, the reduced ceria is re-oxidized with H$_2$O and/or CO$_2$ to produce H$_2$ and/or CO, typically at ambient pressure and temperatures below 1000 °C. The re-oxidized ceria is then recycled back to the reduction step and because the ceria is not consumed in the process, the net reactions are $\text{H}_2\text{O}\rightarrow\text{H}_2+\text{1/2O}_2$ and/or $\text{CO}_2\rightarrow\text{CO}+\text{1/2O}_2$. Because the fuel (H$_2$ and/or CO) and O$_2$ are released in different steps, there is no need for high temperature gas separation or rapid quenching, and because the ceria remains in its solid phase at both the oxidized and the partially reduced state, both reaction steps can take place in the same reactor.

1.2.1 Thermodynamics

Pure stoichiometric CeO$_2$ has a cubic crystal structure with space group Fm3m over the whole temperature range from room temperature to the melting point of around 2475 °C and has a yellowish color [65]. At elevated temperatures and low $p_{O_2}$, the oxidation state partially changes from Ce$^{4+}$ to Ce$^{3+}$. The resulting charge imbalances are compensated by oxygen vacancies and the release of O$_2$, and the color changes to blue or almost black [65]. The nonstoichiometry $\delta$ generally increases with increasing temperature and decreasing oxygen partial pressure $p_{O_2}$. Figure 1.3 shows the equilibrium nonstoichiometry $\delta$ versus oxygen partial pressure $p_{O_2}$ for different temperatures, determined experimentally using thermogravimetric measurements by Panlener et al [63]. As an example, $\delta \approx 0.05$ at $T = 1600$ °C and $p_{O_2} = 10^{-3}$ bar, whereas $\delta < 10^{-5}$ at $T = 900$ °C and $p_{O_2} = 1$ bar. This means that the oxygen exchange capacity per cycle corresponds to $\delta \approx 0.05$ or $3.3 \text{ L kg}_{\text{CeO}_2}^{-1}$ if the reduction and oxidation steps take place under the corresponding conditions and thermodynamic equilibrium is assumed in both reaction steps. At temperatures above 2000 °C, the thermal reduction of CeO$_2$ to Ce$_2$O$_3$ has also been demonstrated, but the process was found to be impractical due to sublimation of reactive material [71].
Equilibrium oxygen nonstoichiometry $\delta$ as a function of the oxygen partial pressure $p_{O_2}$ for various temperatures in the range of 750–1500 °C [63].

Oxidation of partially reduced ceria takes place if the resulting $p_{O_2}$ of the H$_2$O and/or CO$_2$ dissociation reaction is higher than the equilibrium $p_{O_2}$ of ceria at the current state of $\delta$ and temperature. Therefore, the thermodynamic limit for fuel content in the product gas can be calculated for oxidation with H$_2$O or CO$_2$ according to

$$r_{H_2} = \frac{p_{H_2}}{p_{H_2O}} = \frac{K_{H_2O}}{p_{O_2}^{0.5}} \tag{1.7}$$

$$r_{CO} = \frac{p_{CO}}{p_{CO_2}} = \frac{K_{CO_2}}{p_{O_2}^{0.5}} \tag{1.8}$$

where $r_{H_2}$ and $r_{CO}$ are the ratios of fuel to unreacted oxidant in the product gas, $K_{H_2O}$ and $K_{CO_2}$ are the equilibrium constants for the H$_2$O and CO$_2$ dissociation reactions, obtained from FactSage Thermochemical Software and Databases [72], and $p_{O_2}$ is the oxygen partial pressure at thermodynamic equilibrium.
according to Figure 1.3. Assuming a reduction extent of $\delta = 0.05$ and an oxidation temperature of 900 °C, the corresponding $p_{O_2}$ is $6.3 \cdot 10^{-20}$ bar, which results in maximum fuel concentrations in the product gas of around 97% for both $H_2$ and CO. At $T = 900$ °C but $\delta = 0.005$, the maximum fuel concentrations decrease to 9% for CO and 7% for $H_2$, meaning that complete re-oxidation can only be achieved if the oxidant is fed in excess. If oxidation is conducted at $T = 1600$ °C for isothermal operation with $\delta = 0.05$, $p_{O_2}$ is $8.6 \cdot 10^{-4}$ bar and the corresponding maximum fuel concentrations are approximately 1.4% for CO and 0.35% for $H_2$. This means that there is a tradeoff for choosing an optimal oxidation temperature because for high oxidation temperatures, the temperature swing and corresponding heat losses between reduction and oxidation are relatively low, whereas for lower oxidation temperatures the fuel content and thus the quality of the product gas mixture is higher. Correspondingly, complete re-oxidation results in a high fuel yield per cycle but comes at the cost of diluting the product gas with a large amount of unreacted oxidant. It is therefore important to consider the product quality and to account for necessary product gas treatments when comparing different thermochemical processes.

The thermodynamic properties of ceria can be modified by introducing various dopant elements into the ceria lattice. Different dopants such as zirconium and hafnium have been shown to increase the reduction extent $\delta$ at the same temperature and $p_{O_2}$ compared to pure ceria [55, 56, 73, 74]. However, while these dopants can help to increase the reduction extent, they usually deteriorate the oxidation properties. To date, no material is known that outperforms ceria in both the reduction and the oxidation step.

### 1.2.2 Kinetics

During reduction and oxidation, oxygen atoms have to be removed from or introduced into the crystal lattice, and ceria is known for its high oxygen diffusion coefficient [66, 68]. As a result, the ceria reduction reaction in a solar reactor is typically limited by the heating rate or by the oxygen partial pressure in the reactor if the product gas is not efficiently removed. This has been verified experimentally by Furler et al. [50] who showed that the measured
nonstoichiometry \( \delta \) coincides with the thermal equilibrium at different temperatures in an exemplary solar reactor. During oxidation, the gaseous reactants H\(_2\)O and CO\(_2\) adsorb and split into H\(_2\) and CO on the ceria surface. By comparing different porous ceria structures in thermogravimetric analyses and in a solar reactor, it was found that the oxidation rates scale with the specific surface area of these structures [51, 75]. Chueh et al. [48] observed that the oxidation rate of Sm doped ceria strongly increases when depositing Rh to the surface to serve as a catalyst. They concluded that a step involving the surface must be rate-limiting and that bulk oxygen diffusion is much too rapid to have any detrimental impact on fuel production rates. Ackermann et al. [67] analyzed in detail the kinetics of ceria oxidation with CO\(_2\). They observed that oxidation rates increase with increasing temperature up to \( T \approx 520 \, ^\circ\text{C} \), with increasing CO\(_2\) concentration, and also with increasing reduction extent for \( \delta < 0.06 \).

1.2.3 Solar reactors

Various solar reactor concepts have been proposed to affect the ceria redox cycle, including cavity receiver-reactors with rotating [76, 77], moving [78] or stationary [49, 53, 79] bulk ceria structures, and particle reactors with a moving bed [80-82] or an aerosol flow [52] of ceria particles. Figure 1.4 shows a selection of reactor concepts that have been demonstrated experimentally. The concept of an aerosol flow reactor, developed at ETH Zurich, is illustrated in Figure 1.4 (a) [52]. Ceria particles continuously fall through an alumina tube positioned inside an insulated cavity-receiver. In counter-flow, an inert gas is injected from the bottom of the tube, ensuring the separation of evolving oxygen and the reduced ceria particles. A maximum efficiency of \( \eta_{\text{solar-to-fuel}} = 0.56\% \) was calculated for experiments conducted in a high-flux solar simulator, assuming complete re-oxidation of the reduced particles, which was not demonstrated [52]. The sensible heat of the hot ceria particles and the inert gas stream was not recovered. The authors conclude that the reactor concept requires the selection of appropriate particle sizes that avoid radiative heat transfer limitations and of corresponding gas flow rates that enhance gas advection but avoid particle entrainment.
Figure 1.4 (b) shows an isothermal reactor concept developed at the University of Minnesota [79]. Multiple sets of concentric tubes line the wall of the cavity-receiver, with the gap between the concentric tubes filled with a bed of ceria particles. The solar reactor was built and tested experimentally with a slightly adapted design [83]. The reactor was operated at a steady temperature of 1750 K in a high-flux solar simulator at a power input of 4.4 kW. Reduction was performed by lowering the oxygen partial pressure through flushing with nitrogen, and oxidation was initiated by switching from nitrogen to CO\(_2\). Behind the reaction zone, the concentric tubes acted as counter-flow heat exchangers to recover the sensible heat of the hot gases. Stable operation over 45 cycles was shown, but the performance was relatively poor due to the limitations of isothermal operation. When accounting for the energy needed to produce the inert gas nitrogen, an efficiency of \(\eta_{\text{solar-to-fuel}} = 0.72\%\) was measured and CO\(_2\) had to be fed with a large excess during oxidation, which decreases the value of the product gas mixture [83]. The authors therefore conclude that the isothermal approach is not attractive for future developments due to the thermodynamic limitations.

A third reactor concept that addresses solid heat recovery between the high-temperature reduction step and the low-temperature oxidation step is shown in Figure 1.4 (c) [84]. The counter-rotating-ring receiver/reactor/recuperator (CR5) was developed at Sandia National Laboratories. A set of rings of reactive material are directly heated by concentrated solar radiation at the top of the reactor and reduced in an inert gas atmosphere. At the bottom of the reactor, oxidation takes place at lower temperatures with H\(_2\)O and/or CO\(_2\). Adjacent rings are rotated from the reduction zone to the oxidation zone in opposing directions. Thereby, heat is recuperated from the solid phases, as a hot ring moving out of the reduction zone preheats the adjacent rings moving into the reduction zone. The reactor concept was first proposed for ferrites as reactive material, but later also tested with ceria [84-86]. The heat recuperation concept was demonstrated to work, but difficulties arose during the experiments such as cracking of the rotating structures and mixing of gases between the reduction and oxidation zones, which limited the efficiency \(\eta_{\text{solar-to-fuel}}\) to values below 1% [86].
Figure 1.4. Different solar reactor concepts to affect the ceria redox cycle that have been experimentally demonstrated: (a) Indirectly irradiated, falling ceria particles [52]. (b) Indirectly irradiated, stationary bed of ceria particles cycled isothermally [79]. (c) Directly irradiated, rotating reactive rings incorporating heat recovery from solids [84].
This thesis is based on another reactor concept using static, bulk ceria structures that has been pursued and continuously improved at ETH Zurich. A first reactor was developed in a joint collaboration between ETH Zurich, the California Institute of Technology and Paul Scherrer Institute (PSI) [49] and tested with different directly irradiated, porous ceria structures [49-51, 87]. A schematic of the reactor is shown in **Figure 1.5 (a)**. It is a windowed cavity-receiver reactor that was operated with a temperature swing, thereby effecting both steps of the redox cycle in a single and stationary reaction vessel. The reactor was used to perform 243 H₂O/CO₂ co-splitting cycles in a high-flux solar simulator (HFSS), yielding 700 standard liters of syngas (including 30.5% of unreacted CO₂ and 16.5% of the inert gas Ar) with an average efficiency of $\eta_{\text{solar-to-fuel}} = 0.77\%$ [51]. The syngas was collected and processed via Fischer-Tropsch synthesis to a mixture of naphtha, gasoil and kerosene, thereby demonstrating the entire production chain of renewable jet fuel from H₂O and CO₂. The solar reactor was analyzed numerically using a heat and mass transfer model [88], and based on the lessons learnt with the first reactor, ETH Zurich developed a second generation solar reactor that featured superior geometry for a more uniform temperature distribution and an enhanced flow field inside the reactor, as illustrated in **Figure 1.5 (b)** [53]. This cavity-receiver reactor at the 4 kW scale contained a directly irradiated ceria reticulated porous ceramic (RPC) structure. The RPC featured dual-scale porosity, with millimeter-scale pores for efficient radiative heat transfer and micrometer-scale pores to increase the specific surface area for enhanced oxidation kinetics. The solar reactor was operated with a combined temperature and pressure swing. The reactor was tested in a HFSS for CO₂ splitting, and a solar-to-fuel energy conversion efficiency of $\eta_{\text{solar-to-fuel}} = 5.25\%$ was demonstrated as well as, in a separate experiment, a cumulative CO₂-to-CO molar conversion, integrated over oxidation time, that attained a peak value of 65% before oxidation was completed [53]. The combined temperature and pressure swing operation was compared to only a temperature swing operation when conducting the reduction step under atmospheric pressure with a large inert gas flow rate, and it was concluded that the reduction of the oxygen partial pressure by vacuum pumping is more efficient than by the use of an inert gas [53].
Figure 1.5. Schematics of (a) the first generation [50] and (b) the second generation [53] of cavity-receiver reactors for the two-step solar thermochemical ceria cycle developed at ETH Zurich. The former was tested with different porous ceria structures, while the latter featured a ceria reticulated porous ceramic (RPC) structure with dual-scale porosity.
In terms of experimentally demonstrated reactor efficiency, this is the most advanced solar reactor concept, even though there is no heat recovery between the high-temperature reduction step and the oxidation step at lower temperature. It was estimated that 62.8% of the energy input during the reduction step is needed for sensible heating of the solid reactor components (including the ceria RPC), and this energy is mostly lost when the reactor naturally cools down to the oxidation temperature [53]. By implementing solid heat recovery, the efficiency could be significantly increased, as confirmed by various theoretical studies [64, 89, 90]. Brendelberger et al. [91] assessed the potential for heat recovery using a thermal storage unit with a gas as heat transfer fluid. Such a separate storage unit could be coupled to the existing solar reactor technology without any major design changes. Only the operation of the solar reactor would have to be adapted, by adding two additional process steps where the reactor is preheated with hot gas coming from the storage unit before the solar reduction step, and cooled while charging the storage unit after the reduction step, respectively. It was estimated that with such a concept, the necessary solar energy input to the reactor could be decreased by up to 40% [91]. However, this does not correspond to an increase in system efficiency by the same amount, as additional energy would be needed for pumping the heat transfer fluid through the circuit. In addition, such a heat recovery system would increase the overall cycle time and the complexity of the overall system. Nonetheless, the proposed system is relatively simple compared to other heat recovery concepts discussed in literature that usually involve moving high-temperature parts, which is technically very challenging to implement [78, 80, 84, 89, 92, 93].

1.2.4 Ceria structures for cavity-receiver reactors

Different bulk ceria structures have been tested, including electrospun fibers [94], porous monoliths [49], porous felts [87], reticulated porous ceramics (RPC) [50, 51, 75], and additive-manufactured ordered porous structures [95]. An ideal, static bulk structure for a directly irradiated cavity-receiver reactor combines the following characteristics:
- Large pores that enhance the penetration of incoming and internal radiation, resulting in a uniform temperature distribution across the structure when it is heated during the reduction step.
- A high specific surface area that enables fast reaction rates during the oxidation step.
- A relatively high material density to increase the ceria mass loading in the reactor for a high fuel yield per cycle.

These requirements partly contradict each other, but a good tradeoff was found in the form of RPCs with dual-scale porosity, which are also used in this thesis. Such RPCs feature millimeter-scale pores with struts containing micrometer-scale pores. While the millimeter-scale pores enhance volumetric absorption and uniform heating during the reduction step, the micrometer-scale pores within the struts increase the specific surface area for fast reaction rates during the oxidation step. The morphological stability of such RPCs with dual-scale porosity was demonstrated with 227 consecutive redox cycles in a solar reactor [51] and with 500 consecutive cycles in an IR furnace [53]. Recently, the use of additive manufacturing techniques was proposed for the fabrication of porous ceria structures [96]. This offers the possibility of fabricating ordered porous structures with a tailored porosity gradient, which could help to achieve uniform heating and realize volumetric absorption of concentrated solar radiation. However, in order to outperform RPCs with such ordered porous structures, the exact geometry needs to be well optimized.

1.2.5 Efficiency, fuel prices and competitiveness

Thermodynamic analyses predict that for the two-step temperature and pressure swing cycle with ceria, efficiencies approaching $\eta_{\text{solar-to-fuel}} = 20\%$ could be reached even without heat recovery, and with heat recovery $\eta_{\text{solar-to-fuel}} = 30\%$ could theoretically be exceeded [48, 64, 89, 97]. The exact numbers strongly depend on the assumptions used for the calculations, such as reduction and oxidation temperatures, solar concentration ratio, pumping efficiency if the reduction step takes place under vacuum, energy penalties for the production of inert gases and the separation of product gases, and gas and solid heat recovery
effectiveness. So far, the highest experimentally demonstrated efficiency for the ceria cycle is $\eta_{\text{solar-to-fuel}} = 5.25\%$ for CO$_2$ splitting [53], but also this number depends on the chosen system boundaries and the assumptions used for the calculation of energy penalties.

Falter et al. [16] conducted a detailed economic analysis to calculate the expected fuel price for jet fuel production from seawater and ambient air via the solar ceria cycle. The outcome of such economic analyses depends even more on the underlying assumptions. Assuming, amongst other things, a solar tower concentration efficiency of 51.7% and an efficiency of the solar reactor of $\eta_{\text{solar-to-fuel}} = 20\%$ (accounting for the energy needed to separate unreacted CO$_2$ from the product gas mixture), they calculated an overall process efficiency of 5.0% and a price of 2.23 €/L of jet fuel [16]. For more optimistic assumptions (solar reactor efficiency of $\eta_{\text{solar-to-fuel}} = 30\%$, higher annual irradiation at the plant location, lower CO$_2$ and heliostat costs), the price dropped to 1.28 €/L. In a similar study, Kim et al. [98] calculated a minimum selling price of about 1.50 €/L of gasoline equivalent, assuming a conversion efficiency of 20% from unconcentrated sunlight to syngas. In a different study, Falter et al. [99] analyzed the water footprint and the land requirement for solar thermochemical jet fuel production via the ceria cycle. They concluded that both the water footprint and the land requirement are larger than for the best power-to-liquid pathways (i.e. electrolysis powered with electricity from renewable sources), but an order of magnitude lower than for the best biomass-to-liquid pathways, with the added benefit that arid regions are best-suited for the solar thermochemical pathway, therefore not competing with food production [99]. Siegel et al. [100] assert that any thermochemical fuel process must achieve a solar-to-fuel efficiency of 20%, including the optical efficiency of the solar concentrating facility and energy losses associated with processing of the fuel product such as gas separation, to be superior to solar powered low-temperature electrolysis. Depending on the efficiencies of solar concentration and fuel processing, this easily translates into reactor-only efficiencies of 30% and more.
1.3 Thesis goal and outline

This thesis was performed in the framework of the European Union Horizon 2020 project SUN-to-LIQUID. The goal of the SUN-to-LIQUID project was to demonstrate liquid hydrocarbon fuels production from concentrated sunlight, water and CO₂ under real-world conditions and at a relevant scale, using three different subsystems installed in Móstoles, Spain: a high-flux solar concentrating heliostat field and tower, a solar thermochemical reactor system based on the ceria cycle, and a gas-to-liquid conversion plant working with the Fischer-Tropsch process. This thesis deals with the development, commissioning, experimental assessment, and optimization of the solar reactor system. The solar reactor technology is based on ETH’s batch-type cavity-receiver reactor previously introduced (see Figure 1.5), but realized at a roughly tenfold bigger scale.

The thesis is structured in three main chapters, describing the path from reactor development to the successful implementation in the fuel production facility in Spain.

In chapter 2, the design of the solar reactor is presented, including three different reactor cavities assembled as an interlocking structure of ceria RPCs. The solar reactor is tested for CO₂ splitting in a high-flux solar simulator, and conclusions are drawn on how to improve the ceria RPC cavities.

In chapter 3, a numerical heat transfer model of the solar reactor is described. The reactor model was experimentally validated with results from chapter 2 that were obtained in the high-flux solar simulator. A parametric study of crucial operational parameters of the reactor and design variables for the ceria RPC cavity is conducted, and potential paths to improve the reactor technology are discussed.

Chapter 4 presents the solar fuels production facility in Móstoles, Spain. The solar reactor is slightly adapted for the operation in the solar tower, and contains an optimized ceria RPC cavity that was designed and built based on the lessons learnt from the initial testing in the solar simulator and the numerical heat transfer model. The performance of the solar reactor is experimentally assessed and
optimized for maximum solar-to-fuel energy conversion efficiency as well as for optimal fuel composition for the downstream Fischer-Tropsch process. Using optimal operational conditions, 62 consecutive redox cycles are performed with the same ceria RPC cavity to assess the cycling stability and to produce a significant amount of syngas that can be processed on-site to liquid hydrocarbon fuels via Fischer-Tropsch synthesis.

Finally, chapter 5 concludes the thesis with an outlook and recommendations for future research.
2 Design and testing of a 50 kW solar reactor\textsuperscript{1}

In this chapter, the design of the 50 kW solar reactor for pressure and temperature swing thermochemical redox cycling is presented and the reactor is experimentally tested for CO\textsubscript{2} splitting in a high-flux solar simulator. Three different reactor cavities made of an interlocking structure of ceria reticulated porous ceramic (RPC) bricks are tested. The results indicate the benefit of a big ceria mass loading for the mechanical integrity of the RPC cavity, but also highlight that the reactor performance does not increase by adding mass without ensuring effective volumetric absorption of the solar radiation and uniform heating of the ceria. A maximum solar-to-fuel energy conversion efficiency of $\eta_{\text{solar-to-fuel}} = 3.48 \pm 0.08\%$ is measured, with the relatively low efficiency attributed to the limited power of the high-flux solar simulator that is below the design point of the solar reactor, and an experiment with five consecutive CO\textsubscript{2} splitting cycles shows stable operation without observable degradation.

2.1 Solar reactor design and experimental methods

2.1.1 Solar receiver-reactor

The solar reactor is schematically shown in Figure 2.1 (a). It is a cavity-receiver with a circular aperture of 16 cm diameter through which concentrated solar radiation enters. The aperture is sealed with a 12 mm thick circular quartz window that has a diameter of 300 mm. The window is mounted on a water-cooled aluminum front, which is screwed onto the reactor vessel made out of stainless steel. The quartz window is cooled with a continuous flow of compressed air at the outer surface. The steel shell has four lateral ports to introduce thermocouples for temperature measurements. The reactor is insulated with layers of porous Al₂O₃–SiO₂ insulation (Rath, Inc., type KVS 184/400). A detachable insulating jacket made from woven glass fibers and filled with ceramic mat board that covers the outside of the steel shell provides additional insulation. The walls of the cavity consist of an interlocking structure of ceria RPC bricks, approaching the shape of a cylinder with a base. The inner RPC surface is directly exposed to the concentrated solar radiation. Reaction and inert gases enter the reactor through tangential inlet ports behind the window to form a vortex flow that protects the window from the deposition of particles. Between the RPC and the Al₂O₃–SiO₂ insulation, there is a gap of around 10 mm thickness that facilitates gas flow through the reaction cavity. Product gases leave the reactor through a port at the back of the reactor vessel. Figure 2.1 (b) is a photograph of the solar reactor taken from the front. It also shows the copper tubes and nozzles on the bottom right that guide compressed air onto the outer surface of the quartz window to ensure continuous convective cooling.
Figure 2.1. (a) Schematic of the solar reactor. It is a directly irradiated cavity receiver-reactor containing a reticulated porous ceramic (RPC) structure made of ceria. Red arrows indicate gas inlet and outlet. The detachable insulating jacket covering the outside of the steel shell is not shown here. (b) Photograph of the front of the solar reactor.
2.1.2 Ceria RPC structures

**RPC synthesis** – The ceria RPC structures were fabricated with an adapted version of the Schwartzwalder replication method [101]. The main steps of the manufacturing process are illustrated in Figure 2.2. In the first step, organic polyurethane (PU) foams (Foam Partner, Schaumstoff Härti AG) with a porosity of 10 ppi (pores per inch) were cut to the desired shape. The foams were then coated with a ceria-based slurry. The slurry consisted of cerium(IV) oxide powder (Sigma Aldrich, particle size < 5 μm, purity 99.9%), 30 vol% of carbon fibers (Sigrafil, SGL Group, mean fiber length 150 μm), deflocculating agent (Dolapix CE 64), binder (Optapix PA 4G), and deionized water. The exact mixture of the slurry was developed during different projects and is described elsewhere [102, 103]. After immersing the PU foams into the slurry, they were dried in air and sintered in an electrically heated furnace at 1600 °C.

![Polyurethane foam](image1) → ![Coated with slurry](image2) → ![Sintered RPC](image3)

**Figure 2.2.** Manufacturing process of ceria RPCs using the Schwartzwald replication method.

The RPC features dual-scale porosity: millimeter-scale pores with struts containing micrometer-scale pores. This is illustrated in Figure 2.3. The millimeter-scale pores originate from the structure of the PU foam. The organic foam burns out during sintering, resulting in the hollow inner channel of the struts that can be seen in the first inset. The second inset shows the micrometer-scale pores within the strut resulting from the carbon fibers, which also burn out while sintering. The millimeter-scale pores enhance volumetric absorption of concentrated solar radiation during the reduction step, while the micrometer-scale pores within the struts increase the specific surface area which enhances reaction kinetics during the oxidation step [75].
Design of ceria RPC cavities – Three different sets of ceria RPC bricks were installed and tested in the solar reactor. The key parameters of these RPC cavities are summarized in Table 2.1. Cavities #1 and #2 have the same geometric shape, as illustrated in Figure 2.4. The side of these cavities is formed by two octagonal rings, each of which consisting of eight RPC bricks with a thickness of 25 mm. The back consists of a circular centerpiece surrounded by eight wedge-shaped bricks with the same thickness. The difference between cavities #1 and #2 is the RPC porosity, resulting in a different ceria mass loading, while the total volume of the RPCs is identical. The dual-scale porosity $\phi_{\text{dual}}$, defined as the fraction of the volume of all voids over the total volume, is 0.78 for cavity #1, compared to 0.72 for cavity #2. It was calculated by measuring the mass and the total volume of the RPCs. Cavity #3 consists of a larger number of RPC bricks, each having a thickness of 50 mm. The side of the cavity is also formed by two rings, but each ring consisting of thirteen RPC bricks, thereby more closely approximating the shape of a cylinder. The back consists of a circular centerpiece and thirteen wedge-shaped bricks. To manufacture the twice as thick RPC bricks, two PU
foams were stacked on top of each other immediately after coating, because no foams were available at the desired thickness. After drying and sintering, this resulted in single, monolithic RPC bricks. For cavity #3, an additional, third-scale porosity was introduced. The side RPC bricks each featured 28 equally distributed holes with a diameter of 1 cm going halfway through the thickness of the brick. **Figure 2.5 (a)** shows a section view of such an RPC as designed in CAD and **(b)** is a photograph of a fabricated RPC with the additional third-scale pores. In order to manufacture these additional pores, the array of holes was punched into the PU foam forming the top layer of the RPC before coating. However, only half of the side bricks featured this additional porosity, while the other half and the back of the cavity consisted of the standard RPC with dual-scale porosity. The idea behind this new design was to increase the penetration depth of incoming rays to achieve a relatively uniform temperature distribution across the RPC even with the higher thickness. Because of limited resources for manufacturing and testing, only a portion of the cavity was manufactured with this additional porosity, with the main goal of testing the feasibility of manufacturing and the mechanical stability during operation in the solar reactor. Out of the same reason, the size, distribution and quantity of holes was not optimized.

**Table 2.1.** Specifications of the three different RPC cavities installed in the solar reactor.

<table>
<thead>
<tr>
<th>Label</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of RPC bricks per lateral ring</td>
<td>8</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>Porosity specification</td>
<td>Dual-scale porosity</td>
<td>Dual-scale porosity</td>
<td>Partial third-scale porosity</td>
</tr>
<tr>
<td>RPC thickness $t_{RPC}$ (mm)</td>
<td>25</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Dual-scale porosity $\phi_{dual}$</td>
<td>0.78</td>
<td>0.72</td>
<td>0.76</td>
</tr>
<tr>
<td>Ceria RPC mass $m_{RPC}$ (kg)</td>
<td>18.3</td>
<td>23.3</td>
<td>42.9</td>
</tr>
</tbody>
</table>
Figure 2.4. Different RPC cavity geometries tested in the solar reactor. (a) and (c) show the two different geometries as designed with CAD, while (b) and (d) are photographs of the RPCs installed in the reactor. Cavities #1 and #2 both have the same octagonal shape but differ in RPC porosity, while cavity #3 consists of more and thicker RPC bricks.
Figure 2.5. Detail view of a RPC brick from cavity #3 showing the partially implemented third-scale porosity. (a) is a section view of the brick as designed with CAD, while (b) is a photograph showing a section of a newly manufactured brick from the top.

Three-point bend testing – Apart from testing the RPCs in the solar reactor, the mechanical strength of these RPCs with different porosities and thicknesses was also analyzed with three-point bend testing using a type BT1 Zwick ultimate testing machine. RPC bricks with similar size as the ones installed in the solar reactor where placed on two 20 mm diameter support rods. A 20 mm diameter stamping rod was displaced at a rate of 1 mm min$^{-1}$ until the RPC failed by cracking into two pieces and the force at failure was recorded.

2.1.3 Experimental setup and procedure

The setup for the solar reactor experiments is schematically illustrated in Figure 2.6. Experiments were performed at the high-flux solar simulator (HFSS) of the Paul Scherrer Institute (PSI). An array of ten xenon arc lamps, close-coupled to truncated ellipsoidal reflectors, provides an external source of intense thermal radiation, mostly in the visible and infrared spectra, which closely approximates the radiative properties of highly concentrating solar systems such as towers and dishes [104]. The radiative flux distribution at the aperture plane of the solar reactor was optically measured using a calibrated CCD camera focused onto a water-cooled, Al$_2$O$_3$ plasma-coated Lambertian target. The total solar radiative power input $P_{\text{solar}}$ was obtained by integration of the measured flux distribution in the aperture plane, including adjusting for the absorption and reflection losses at the quartz window. Although the reactor was designed for higher power input, a maximum of $P_{\text{solar}} = 32.2$ kW was used due to limited power of the solar
Design and testing of a 50 kW solar reactor

simulator, corresponding to a solar concentration ratio of $C = 1602 \text{ suns}^2$. The temperature of the reacting ceria was monitored at four positions distributed over the back surface of the RPC using B-type thermocouples. The average of these temperature measurements was defined as the nominal RPC temperature $T_{\text{RPC,nom}}$. The temperature of the lateral Al$_2$O$_3$–SiO$_2$ insulation was measured at three different depths using K-type thermocouples. K-type thermocouples were also used to measure the temperatures of the outer lateral surfaces of the reactor shell and the insulating jacket. Gas flow rates were regulated using electronic mass flow controllers (Bronkhorst, EL-FLOW Select). The pressure inside the reactor was measured at the gas outlet using a Pirani gauge sensor combined with a capacitance diaphragm vacuum gauge (Leybold, THERMOVAC TTR 101). A dry, multi-stage roots vacuum pump (Pfeiffer Vacuum, ACP 40) was attached to the outlet port of the solar reactor via two parallel evacuation valves. A membrane valve was used to slowly evacuate the reactor at the beginning of the reduction step (path shown by the red arrows in Figure 2.6), and a gate valve with bigger nominal diameter was opened once the pressure was sufficiently low ($< 50 \text{ mbar}$). During the oxidation step (path shown by the blue arrows in Figure 2.6), the vacuum pump was bypassed by use of a manual membrane valve. The composition of the product gas was continuously (frequency 1 Hz) analyzed downstream using an electrochemical sensor for O$_2$, and IR detectors for CO and CO$_2$ (Siemens, Ultramat 23). The gas composition was verified by gas chromatography (Agilent, 490 Micro GC) with a measurement frequency of 0.005 Hz.

---

2 The solar concentration ratio $C$ is defined as $C = P_{\text{solar}} / (I \cdot A)$, where $P_{\text{solar}}$ is the solar radiative power intercepted by the aperture area $A$, and $I$ is the direct normal solar irradiation. $C$ is often expressed in units of “suns” when normalized to $I = 1 \text{ kW m}^{-2}$. 

Figure 2.6. Schematic of the experimental setup. During the endothermic reduction step, Ar flow is used to protect the quartz window and is pumped out together with the released O\textsubscript{2}, while the reactor is under vacuum and irradiated with concentrated solar radiation. During the exothermic oxidation step, the ceria is re-oxidized with CO\textsubscript{2}, therefore producing CO.
In Figure 2.7, the solar reactor is shown in operation. During an experimental run, the solar reactor was first slowly preheated with a radiative power input $P_{\text{solar}}$ between 5 and 10 kW for approximately 75 minutes, followed by a slow pre-cycle. During a pre-cycle, the reactor was heated with $P_{\text{solar}} = 10–25$ kW ramping up, for approximately 30 minutes until the nominal reduction temperature was reached. The pre-cycle was terminated by closing the shutters of the solar simulator (thereby effecting $P_{\text{solar}} = 0$ kW) and letting the reactor naturally cool down to the nominal oxidation temperature. The ceria was fully re-oxidized using CO$_2$. Once the nominal RPC temperature reached the defined reduction start temperature, the primary reduction step was initiated with constant $P_{\text{solar}}$ in the range of 26.9–32.2 kW, while the reactor was evacuated using the vacuum pump. The total pressure in the reactor during the reduction step was in the range of 3–9 mbar, depending on the current rate of oxygen release. To protect the quartz window from deposition of sublimated ceria [50] and to govern the fluid flow field when operating under vacuum conditions, an argon flow rate of 5.35 L min$^{-1}$ (SLPM; volume flow rate calculated at 273.15 K and 101’325 Pa) was introduced to the reactor directly behind the window. When the variable reduction end temperature was reached, re-oxidation was initiated by removing input power and repressurizing the reactor with CO$_2$. After the nominal RPC temperature fell to the oxidation start temperature by natural cooling, CO$_2$ was flown through the reactor at a constant rate in the range of 34–150 L min$^{-1}$ until the ceria was fully re-oxidized, producing a mixed flow in the outlet comprised of CO and unreacted CO$_2$. 
Figure 2.7. Photographs of the solar reactor in operation: (a) the high-flux solar simulator heating up the solar reactor during the reduction step; (b) the irradiated front of the reactor; (c) the glowing ceria RPC bricks seen through the reactor’s aperture while cooling down shortly after the end of the reduction step.
2.1.4 Solar-to-fuel energy conversion efficiency

A key performance indicator of the solar reactor is the solar-to-fuel energy conversion efficiency \( \eta_{\text{solar-to-fuel}} \), which is defined as

\[
\eta_{\text{solar-to-fuel}} = \frac{Q_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{pump}} + Q_{\text{inert}}} \tag{2.1}
\]

The energy content of the fuel produced, \( Q_{\text{fuel}} \), is

\[
Q_{\text{fuel}} = \Delta H_{\text{fuel}} \cdot \int r_{\text{fuel}} \, dt \tag{2.2}
\]

In the case of \( \text{CO}_2 \) splitting, \( \Delta H_{\text{fuel}} \) is the heating value of \( \text{CO} \) \((\Delta H_{\text{CO}} = 283 \, \text{kJ mol}^{-1})\), and \( r_{\text{fuel}} \) is the molar rate of \( \text{CO} \) produced. Assuming complete re-oxidation, the energy content of the fuel produced in a cycle can also be calculated as \( Q_{\text{fuel}} = \Delta H_{\text{fuel}} \cdot 2 \int r_{\text{O}_2} \, dt \), where \( \int r_{\text{O}_2} \, dt \) is the rate of released oxygen integrated over the reduction step. \( Q_{\text{solar}} \) is the total solar energy input integrated over the endothermic reduction, and is defined as

\[
Q_{\text{solar}} = \int P_{\text{solar}} \, dt \tag{2.3}
\]

where \( P_{\text{solar}} \) is the solar radiative power input through the reactor’s aperture, plus absorption and reflection losses at the quartz window. \( Q_{\text{pump}} \) and \( Q_{\text{inert}} \) are the energy penalties associated with vacuum pumping and the consumption of the inert gas \( \text{Ar} \) during the reduction step, respectively, and are calculated as suggested in reference [53]. The vacuum pumping energy is calculated as the thermodynamic minimum pumping work divided by a heat-to-work energy conversion efficiency, \( \eta_{\text{heat-to-work}} \) (assumed 0.4 [80, 105]), and a pressure dependent vacuum pumping efficiency, \( \eta_{\text{pump}} \), according to

\[
Q_{\text{pump}} = \frac{1}{\eta_{\text{heat-to-work}}} \cdot \int \frac{R \cdot T_{\text{pump}}}{\eta_{\text{pump}}(P_{\text{reactor}}(t))} \cdot \dot{n}(t) \cdot \ln \left( \frac{p_{\text{atm}}}{p_{\text{reactor}}(t)} \right) \, dt \tag{2.4}
\]

where \( \dot{n}(t) \) is the molar flow rate pumped out of the reactor, consisting of the inert gas \( \text{Ar} \) injected to the reactor, the \( \text{O}_2 \) released by ceria, and the gas evacuated from the reactor during transient change of pressure, \( R \) is the universal gas
constant \((R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})\), \(T_{\text{pump}}\) is the pump temperature (assumed 298.15 K), and \(p_{\text{atm}}\) and \(p_{\text{reactor}}\) are atmospheric and reactor pressure, respectively. The pumping efficiency, derived by Brendelberger et al. [105], is based on the analysis of a multi-stage industrial vacuum pump arrangement from Pfeiffer vacuum and calculated as

\[
\eta_{\text{pump}}(p_{\text{reactor}}(t)) = 0.07 \cdot \log \left( \frac{p_{\text{reactor}}(t)}{p_{\text{atm}}} \right) + 0.4
\]  

(2.5)

The energy required for the separation of the inert gas Ar is defined as

\[
Q_{\text{inert}} = \frac{1}{\eta_{\text{heat-to-work}}} E_{\text{inert}} \int r_{\text{inert}} \, dt
\]  

(2.6)

where \(E_{\text{inert}}\) is the work required for inert gas separation (assumed 20 kJ per mole of Ar [106]) and \(r_{\text{inert}}\) is the flow rate of the inert gas Ar during reduction. Note that \(\eta_{\text{solar-to-fuel}}\) is weakly dependent on the assumptions used for the calculation of the two energy penalties, because \(Q_{\text{solar}}\) is roughly two orders of magnitude larger than \(Q_{\text{pump}}\) and \(Q_{\text{inert}}\).

### 2.2 Experimental results and discussion

A typical cycle for CO\(_2\) splitting with the RPC cavity #1 is illustrated in Figure 2.8. It shows the nominal RPC temperature, the reactor pressure as well as the O\(_2\) and CO evolution rates as a function of time. The experimental conditions and measured results of the same experiment are summarized in Table 2.2. During the reduction step at \(P_{\text{solar}} = 30.5\) kW and under vacuum pressure, the RPC temperature rapidly increased from 698 °C to 1504 °C in 12.4 min, corresponding to a mean heating rate of 65 °C min\(^{-1}\). The rate of released O\(_2\) increased with increasing temperature to a maximum of 4.5±0.1 L min\(^{-1}\). Due to limited pumping power, the reactor pressure slightly increased the more O\(_2\) was released, reaching 8.4±1.2 mbar at the end of the reduction step. When \(P_{\text{solar}}\) was turned off at the end of the reduction step, the O\(_2\) release stopped and the reactor was repressurized with CO\(_2\) while the RPC temperature started decreasing. Within 13.3 min, the reactor naturally cooled down to 1000 °C, which is when the oxidation step was initiated by flowing 68.0 L min\(^{-1}\) of CO\(_2\) through the reactor. Shortly afterwards, a peak CO evolution rate of 14.4±0.3 L min\(^{-1}\) was
measured. Integrated over the entire oxidation step, a total of 66.4±6.3 L CO was produced. The molar ratio of CO to O₂ was 2.21±0.26, implying complete re-oxidation of the reduced ceria. The solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$ was 3.26±0.07%. Previous work on a similar, but significantly smaller solar reactor configuration at the 4 kW scale resulted in $\eta_{\text{solar-to-fuel}} = 5.25\%$ for CO₂ splitting [53]. The relatively low efficiency is attributed to the limited power of the high-flux solar simulator. Significantly higher efficiencies are expected for the operation of the solar reactor in the solar tower in Spain at $P_{\text{solar}} = 50$ kW.

![Graph](image)

**Figure 2.8.** Nominal RPC temperature, reactor pressure and O₂ and CO evolution rates as a function of time during a typical CO₂ splitting cycle with the RPC cavity #1. Experimental conditions during reduction: $P_{\text{solar}} = 30.5$ kW, $T_{\text{red, start}} = 698$ °C, $T_{\text{red, end}} = 1504$ °C, $\dot{V}_{\text{Ar}} = 5.35$ L min⁻¹ at $P_{\text{reactor}} < 9$ mbar. Experimental conditions during oxidation: $P_{\text{solar}} = 0$ kW, $T_{\text{ox, start}} = 1000$ °C, $T_{\text{ox, end}} = 696$ °C, $\dot{V}_{\text{CO₂}} = 68.0$ L min⁻¹ at atmospheric pressure.
Table 2.2. Experimental conditions and results of a typical CO$_2$ splitting cycle with the ceria RPC cavity #1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar radiative power input during reduction</td>
<td>$P_{\text{solar}}$</td>
<td>30.5</td>
<td>kW</td>
</tr>
<tr>
<td>Reduction start temperature</td>
<td>$T_{\text{red,start}}$</td>
<td>698</td>
<td>°C</td>
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<tr>
<td>Reduction end temperature</td>
<td>$T_{\text{red,end}}$</td>
<td>1504</td>
<td>°C</td>
</tr>
<tr>
<td>Oxidation start temperature</td>
<td>$T_{\text{ox,start}}$</td>
<td>1000</td>
<td>°C</td>
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<tr>
<td>Oxidation end temperature</td>
<td>$T_{\text{ox,end}}$</td>
<td>696</td>
<td>°C</td>
</tr>
<tr>
<td>Ar flow rate during reduction</td>
<td>$\dot{V}_{\text{Ar}}$</td>
<td>5.35</td>
<td>L min$^{-1}$</td>
</tr>
<tr>
<td>CO$_2$ flow rate during oxidation</td>
<td>$\dot{V}_{\text{CO}_2}$</td>
<td>68.0</td>
<td>L min$^{-1}$</td>
</tr>
<tr>
<td>Reactor pressure at end of reduction</td>
<td>$p_{\text{red}}$</td>
<td>8.4±1.2</td>
<td>mbar</td>
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<tr>
<td>Reduction duration</td>
<td>$t_{\text{red}}$</td>
<td>12.4</td>
<td>min</td>
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<tr>
<td>Oxidation duration</td>
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<tr>
<td>Peak O$_2$ evolution rate</td>
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<td>Total amount of O$_2$ released</td>
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<td>Average nonstoichiometry of ceria</td>
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<td>Peak CO evolution rate</td>
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<tr>
<td>Total amount of CO produced</td>
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<td>Average conversion of CO$_2$ to CO</td>
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<td>Molar ratio CO/O$_2$</td>
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<td>kJ</td>
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<td>Inert gas Ar separation energy</td>
<td>$Q_{\text{inert}}$</td>
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<td>kJ</td>
</tr>
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<td>Solar-to-fuel energy conversion efficiency</td>
<td>$\eta_{\text{solar-to-fuel}}$</td>
<td>3.26±0.07</td>
<td>%</td>
</tr>
</tbody>
</table>
2.2.1 Variation of the solar radiative power input

To experimentally assess the influence of different solar radiative power inputs on the performance of the solar reactor, we conducted CO₂ splitting cycles with the RPC cavity #2 at three levels of $P_{\text{solar}}$ ranging from 26.9 kW to 31.0 kW. Lower levels of $P_{\text{solar}}$ are unfeasible because a certain amount of power is needed to reach the reduction end temperature in a reasonable amount of time, while the upper limit was set by the power limit of the high-flux solar simulator. The nominal RPC temperature as well as the O₂ and CO evolution rates are shown as a function of time in Figure 2.9 (a) for $P_{\text{solar}} = 26.9$, 29.2, and 31.0 kW. Reduction and oxidation temperatures were kept constant at $T_{\text{red, end}} = 1461–1464 \, ^\circ\text{C}$, $T_{\text{ox, start}} = 1000 \, ^\circ\text{C}$, and a sufficiently low oxidation end temperature of $T_{\text{ox, end}} = 795 \, ^\circ\text{C}$ to assure complete re-oxidation with CO₂.

Figure 2.9 (b) shows the volume of produced O₂ and CO, the reduction time and $\eta_{\text{solar-to-fuel}}$ as a function of $P_{\text{solar}}$ for these three cycles. The amount of fuel produced per cycle is relatively stable with no visible trend, due to the identical reduction end temperatures. The reduction time though decreases significantly from 30.7 min at $P_{\text{solar}} = 26.9$ kW to 22.0 min at $P_{\text{solar}} = 31.0$ kW. As a result, $\eta_{\text{solar-to-fuel}}$ increases from $2.03 \pm 0.03\%$ at $P_{\text{solar}} = 26.9$ kW to $2.34 \pm 0.06\%$ at $P_{\text{solar}} = 31.0$ kW. The positive trend of increasing $\eta_{\text{solar-to-fuel}}$ with increasing $P_{\text{solar}}$ is mainly attributed to lower heat losses by reradiation through the aperture and conduction through the reactor insulation during the shorter reduction times, and highlights the great potential for performance increase when the reactor is operated at higher $P_{\text{solar}}$. 
Figure 2.9. (a) Nominal RPC temperature and O\textsubscript{2} and CO evolution rates as a function of time for three CO\textsubscript{2} splitting cycles at different solar radiative power input $P_{\text{solar}}$ during the reduction step, conducted with the RPC cavity #2. (b) Volume of produced O\textsubscript{2} and CO, reduction time $t_{\text{red}}$ and efficiency $\eta_{\text{solar-to-fuel}}$ of the same cycles as a function of $P_{\text{solar}}$. 
2.2.2 Comparison of different RPC cavities

The performance of the three different ceria RPC cavities during similar CO$_2$ splitting cycles is directly compared in Figure 2.10. As specified in Table 2.1, cavities #1 and #2 had the same geometric shape, but different dual-scale porosities of the RPC and resulting ceria RPC mass loadings ($\phi_{\text{dual}} = 0.78$ and $m_{\text{RPC}} = 18.3$ kg for cavity #1, and $\phi_{\text{dual}} = 0.72$ and $m_{\text{RPC}} = 23.3$ kg for cavity #2, respectively). The main difference of cavity #3 was the doubled thickness of the RPC structures (50 mm instead of 25 mm), resulting in a much higher mass loading of $m_{\text{RPC}} = 42.9$ kg. Figure 2.10 (a) shows the nominal RPC temperature as well as the O$_2$ and CO evolution rates as a function of time for the three cases. $P_{\text{solar}}$ was equal to 31 kW in all three cases. The temperature gradient throughout the thickness of the RPC during the reduction step, with the highest temperature at the directly irradiated front surface and the lowest temperature at the back surface where the temperature is measured, increases both with decreasing RPC porosity and with increasing RPC thickness [107, 108]. Therefore, the reduction end temperature was set to 1512 °C for cavity #1, 1461 °C for cavity #2 and 1440 °C for cavity #3 in an attempt to reach similar maximum temperatures of the RPC structures, $T_{\text{RPC,max}}$, for all cases. These temperatures were chosen without knowing the actual values of $T_{\text{RPC,max}}$, resulting in cycles that are not perfectly comparable, but still serve as a good indicator for performance. The oxidation start temperature was 1000 °C for all cases. The flow rate of CO$_2$ during oxidation and the oxidation end temperature were varied, because with increasing mass loading, the solar reactor was cooling slower during oxidation, and complete re-oxidation was already achieved at higher temperatures.

In Figure 2.10 (b), the volume of produced O$_2$ and CO, the reduction time and $\eta_{\text{solar-to-fuel}}$ is shown as a function of $m_{\text{RPC}}$ for the three RPC cavities. Compared to RPC cavity #1, the reduction time of cavity #2 increased by 71% from 12.9 min to 22.0 min, although the mass only increased by 27% from 18.3 kg to 23.3 kg. Apart from the higher thermal mass, we attribute the longer reduction time of cavity #2 to the lower porosity that leads to a smaller penetration depth of incident radiation and less uniform heating of the RPC. The amount of fuel produced increased by 24% from 70.5±6.7 L for cavity #1 to 87.7±9.1 L for
cavity #2. As a consequence, a lower efficiency was achieved with cavity #2 ($\eta_{\text{solar-to-fuel}} = 2.34\pm0.06\%$ compared to $\eta_{\text{solar-to-fuel}} = 3.34\pm0.06\%$ for cavity #1).

The reduction time of the RPC cavity #3 was again significantly higher. Compared to cavity #1 it nearly tripled from 12.9 min to 35.5 min, while the mass increase was 134%. The amount of CO produced also increased from 70.5±6.7 L to 161.6±19.0 L, but this increase was not enough to compensate for the much longer reduction time. As a consequence, $\eta_{\text{solar-to-fuel}}$ was 2.36±0.06% for cavity #3, compared to $\eta_{\text{solar-to-fuel}} = 3.34\pm0.06\%$ for cavity #1.

These results indicate that without effective volumetric absorption of the solar radiation inside the RPC structure to ensure uniform heating, increasing the ceria mass loading does not result in increased reactor performance due to slower heating. It is important to note though that the presented results could change when the reactor is operated differently, for example at higher $P_{\text{solar}}$. Most importantly, when designing a RPC cavity for the solar reactor, not only the performance of a single cycle should be considered, but also the stability over many consecutive cycles. This is discussed in more detail in the next section.
Figure 2.10. (a) Nominal RPC temperature and O\textsubscript{2} and CO evolution rates as a function of time for a CO\textsubscript{2} splitting cycle each with three different RPC cavities (see Table 2.1 for specifications). (b) Volume of produced O\textsubscript{2} and CO, reduction time \( t_{\text{red}} \) and efficiency \( \eta_{\text{solar-to-fuel}} \) of the same cycles as a function of the ceria RPC mass \( m_{\text{RPC}} \) (RPC cavity #1: 18.3 kg; #2: 23.3 kg; #3: 42.9 kg).
2.2.3 Stability observations

**Consecutive cycling** – To assess the stability of the reactor, five consecutive cycles were performed with the RPC cavity #1 with almost equal operational conditions during the different cycles. The nominal RPC temperature, reactor pressure and O\textsubscript{2} and CO evolution rates of these cycles are shown in Figure 2.11. \(P_{\text{solar}}\) was slightly increased from 30.5 kW in the first cycle to 32.2 kW in the fifth cycle. Reduction and oxidation temperatures and inlet flow rates were: \(T_{\text{red, start}} = 696–700^\circ\text{C}\), \(T_{\text{red, end}} = 1504–1513^\circ\text{C}\), \(T_{\text{ox, start}} = 1000^\circ\text{C}\), \(T_{\text{ox, end}} = 696–700^\circ\text{C}\), \(\dot{V}_{\text{Ar}} = 5.35 \text{ L min}^{-1}\), \(\dot{V}_{\text{CO}_2} = 68.0 \text{ L min}^{-1}\).

The reactor showed stable performance without observable degradation. The amount of produced CO varied between 66.4±6.3 L and 70.7±6.8 L per cycle. A slight increase of \(\eta_{\text{solar-to-fuel}}\) was observed with increasing cycle number, with \(\eta_{\text{solar-to-fuel}} = 3.26±0.07\) for the first cycle and \(\eta_{\text{solar-to-fuel}} = 3.48±0.08\) for the last cycle, which is attributed to the slightly increased power input \(P_{\text{solar}}\).

For the long-term operation of the solar reactor in the solar tower in Spain or a future commercial application, stable performance over a much larger number of cycles is crucial. Long-term stability of a ceria RPC with dual-scale porosity was demonstrated by Marxer et al. [53] in 500 consecutive redox cycles using an IR furnace. The O\textsubscript{2} yield was constant throughout the cycling, and scanning micrographs before and after cycling revealed that the micrometer-sized pores within the struts of the RPC were preserved. Apart from chemical and mechanical stability on the small scale, mechanical stability on the scale of a RPC brick is equally important. Due to the self-supporting design of the solar reactors’ RPC cavity consisting of multiple separate RPC bricks, the failure of a single brick could lead to a collapse of the entire cavity and needs to be avoided.
Figure 2.11. Nominal RPC temperature, reactor pressure and O\textsubscript{2} and CO evolution rates as a function of time for five consecutive CO\textsubscript{2} splitting cycles with RPC cavity #1. Experimental conditions during reduction: \( P_{\text{solar}} = 30.5–32.2\,\text{kW}, T_{\text{red, start}} = 696–700\,\text{°C}, T_{\text{red, end}} = 1504–1513\,\text{°C}, \dot{V}_{\text{Ar}} = 5.35\,\text{L min}^{-1} \) at \( p_{\text{reactor}} < 9\,\text{mbar} \). Experimental conditions during oxidation: \( P_{\text{solar}} = 0\,\text{kW}, T_{\text{ox, start}} = 1000\,\text{°C}, T_{\text{ox, end}} = 696–700\,\text{°C}, \dot{V}_{\text{CO}} = 68.0\,\text{L min}^{-1} \) at atmospheric pressure.
**Three-point bend testing** – The mechanical strength of RPCs with different porosities and thicknesses was assessed with three-point bend testing. The methodology is described in section 2.1.2. **Figure 2.12** shows the force at failure of different RPC bricks as a function of the dual-scale porosity $\phi_{\text{dual}}$ for the two different RPC thicknesses of $t_{\text{RPC}} = 25$ mm and $50$ mm. A clear trend of increasing force at failure and consequently increasing mechanical strength of the RPCs is visible with decreasing porosity $\phi_{\text{dual}}$, as indicated by the dashed power function fit of the measurements with $t_{\text{RPC}} = 25$ mm. Doubling $t_{\text{RPC}}$ to $50$ mm also resulted in a drastic increase of the force at failure compared to RPCs with similar porosities at $t_{\text{RPC}} = 25$ mm.

![Force at failure measured with three-point bend testing as a function of the dual-scale porosity $\phi_{\text{dual}}$ of various RPC bricks with thickness $t_{\text{RPC}}$ of 25 mm and 50 mm. The dashed line is a power function fit of the measurements with $t_{\text{RPC}} = 25$ mm, showing a clear trend of increasing force at failure with decreasing porosity.](image)

**Visual observations** – Photographs of RPC bricks after testing in the solar reactor are shown in **Figure 2.13**. (a) and (b) are photographs of a brick from RPC cavity #2. Within the indication bars is a crack that formed due to mechanical stresses during cycling. The formation of such cracks was found to be inevitable to some extent, but can be minimized by using stronger RPC bricks. Most importantly,
the self-supporting structure of an RPC cavity needs to be optimized such that it can withstand the formation of such cracks without collapsing.

**Figure 2.13** (c) shows a brick from cavity #3 that delaminated into two separate parts at the interface originating from the layering of two polyurethane foams during the manufacturing process. Although such delamination did not lead to a collapse of the cavity, it is detrimental to its structural integrity and represents a drawback of the fabrication method of thicker, double-layered RPCs. No indication of decreased stability due to the third-scale porosity partially incorporated into cavity #3 was found.

![Figure 2.13](image)

**Figure 2.13.** Photographs of RPC bricks after testing in the solar reactor. (a) and (b) show the side and top view of a brick from RPC cavity #2 with a crack that formed within the indication bars. (c) shows the side view of a brick from cavity #3 which delaminated into two parts.

From comparing the two different cavity geometries tested, it was concluded that assembling the side of the cavity out of thirteen bricks as in RPC cavity #3 is beneficial compared to the octagonal design of cavities #1 and #2. A low number of side parts results in a sharp contact angle and decreases the likelihood of a part to slip out of its position, but increases the width of a single part and the load due to bending. Conversely, using many side parts reduces the risk of failure in bending, but the number of parts is limited to ensure a sufficient contact angle, and an optimum was found to be somewhere in the low two-digit range.
Based on the results from the present chapter, the following conclusions were drawn on the design of RPC cavities:

- There is a trade-off between mechanical strength and cycling performance of a ceria RPC cavity. A general trend between low porosity and high thickness of the RPC, both resulting in higher mass loading, and increasing mechanical strength was observed. On the other hand, after exceeding a certain limit, adding more mass without ensuring effective volumetric absorption of the solar radiation and uniform heating of the ceria does not result in an improved reactor performance.

- Adding a third scale of porosity to the RPC was shown to be possible and could help to ensure more uniform heating of the ceria, but it complicates the fabrication process and a performance increase can only be expected if the structure is thoroughly optimized, for example with a numerical model.

- Manufacturing thicker RPC bricks by stacking two polyurethane foams on top of each other was shown to be feasible, but should be avoided due to possible delamination of the two layers during cycling in the solar reactor.

- Assembling the side rings of the cavity out of more than eight single bricks is beneficial for stability, with an optimum somewhere in the low two-digit number of bricks.
2.3 Summary and conclusions

The design of a scaled-up ceria RPC solar reactor for pressure and temperature swing thermochemical redox cycling was presented. The performance of the solar reactor for CO₂ splitting was experimentally assessed in a high-flux solar simulator. Three different ceria cavities made of an interlocking structure of RPC bricks with different porosities, thicknesses, and geometries were designed and tested. The results indicate that lower porosity and higher thickness, both resulting in a higher ceria mass loading, are generally beneficial for the mechanical integrity of the RPC cavity, but the addition of mass without ensuring effective volumetric absorption of the solar radiation and uniform heating of the ceria does not increase the reactor performance. A maximum solar-to-fuel energy conversion efficiency of $\eta_{\text{solar-to-fuel}} = 3.48\pm0.08\%$ was measured at the limited maximum power of $P_{\text{solar}} = 32.2$ kW, but the direct comparison of cycles at different power levels revealed a trend of increasing efficiency with increasing $P_{\text{solar}}$. This trend highlights the great potential for performance increase when the solar reactor is operated at its design point of $P_{\text{solar}} = 50$ kW in the solar tower in Spain. An extended experiment with five consecutive CO₂ splitting cycles revealed stable operation over multiple cycles without observable degradation.
3 Heat transfer modelling of the solar reactor

To analyze the performance of the previously presented solar reactor and to gain insight into improved design and operational conditions, a transient heat transfer model of the solar reactor was developed and implemented in ANSYS CFX, which is presented in this chapter. The numerical model couples the incoming concentrated solar radiation using Monte Carlo ray tracing, incorporates the reduction chemistry by assuming thermodynamic equilibrium, and accounts for internal radiation heat transfer inside the porous ceria by applying effective heat transfer properties. The model was experimentally validated using data acquired in a high-flux solar simulator, where temperature evolution and oxygen production results from model and experiment agreed well. The numerical results indicate the prominent influence of solar radiative input power, where increasing it substantially reduces reduction time of the ceria structure. Consequently, the model predicts a solar-to-fuel energy conversion efficiency of >6% at a solar radiative power input of 50 kW; efficiency >10% can be obtained provided the RPC macroporosity is substantially increased and better volumetric absorption and uniform heating is achieved. Managing the ceria surface temperature during reduction to avoid sublimation remains a critical challenge for direct absorption solar receiver-reactors.

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3.1 Solar reactor configuration and experimental setup

The solar reactor was introduced in section 2.1 of the previous chapter. The reactor parts relevant for modelling are schematically shown in Figure 3.1 and are briefly summarized here.

The solar reactor has a water-cooled aluminum front (region 1) with a circular aperture of 16 cm diameter through which concentrated solar radiation enters. The aperture is sealed with a 12 mm thick circular quartz window that has a diameter of 300 mm. The aluminum front is attached to the reactor shell (region 2), which is made out of stainless steel (316L). The outside of the shell is insulated with a jacket (region 3) made from woven glass fibers and filled with
ceramic mat board. The inside of the reactor is insulated with KVS184/400 (Rath, Inc.), which is primarily comprised of 80% Al$_2$O$_3$ and 20% SiO$_2$ (region 4). The reaction cavity (region 6) is assembled with an interlocking structure of ceria RPC bricks (region 5). The ceria bricks have a thickness denoted $t_{\text{RPC}}$. Between the RPC and the Al$_2$O$_3$–SiO$_2$ insulation, there is a 10 mm gap (region 7) which facilitates gas flow through the reaction cavity.

The experimental setup (Figure 2.6) and procedure was described in detail in section 2.1.3 of the previous chapter. The positions of the temperature measurements are indicated in Figure 3.1. $T_{B,1}$–$T_{B,3}$ denote the measurement positions of B-type thermocouples at the back surface of the RPC. The nominal RPC temperature $T_{\text{RPC,nom}}$ is defined as the average of these three temperature measurements. The temperature of the lateral Al$_2$O$_3$–SiO$_2$ insulation ($T_{K,1}$–$T_{K,3}$) as well as the outer lateral surfaces of the reactor shell ($T_{K,4}$) and the insulating jacket ($T_{K,4}$) were measured with K-type thermocouples.

### 3.2 Heat transfer analysis

The solar receiver-reactor, which features inherent axial symmetry, was simulated using a two-dimensional axisymmetric heat transfer model implemented in the commercial CFD software ANSYS CFX (release 17.0). The aluminum front, steel shell, insulating jacket and Al$_2$O$_3$–SiO$_2$ insulation are modelled as solid domains. The cavity and the open region behind the RPC are modelled as fluid domains that are non-participating in radiation. During the reduction step the fluid is assumed to be stationary, as previous modelling results have shown that the contribution of convection to heat transfer is negligible, especially while operating under vacuum [88]. The ceria RPC is modelled as a homogeneous and radiatively participating porous media.

#### 3.2.1 Governing equations

As the fluid domains are assumed to be stationary, the system governing equations are reduced to only the energy conservation equation. For the fluid and the solid domains, the energy conservation equation is

$$\frac{\partial}{\partial t} (\rho h) = \nabla \cdot (k \nabla T)$$

(3.1)
where $\rho$ is the density, $h$ is the enthalpy, and $k$ is the thermal conductivity. The energy conservation equation for the solid phase of the porous RPC domain is

$$
\frac{\partial}{\partial t} ((1 - \phi_{\text{dual}}) \rho h) = \nabla \cdot (k_{\text{eff}} \nabla T) + S_{\text{solar}} + S_{\text{reaction}} + Q_{\text{sf}}
$$

(3.2)

where $\phi_{\text{dual}}$ is the dual-scale porosity of the RPC, $k_{\text{eff}}$ is its effective thermal conductivity, $S_{\text{solar}}$ is the source term accounting for the absorbed incoming solar radiation from the HFSS, and $S_{\text{reaction}}$ is the energy sink accounting for the endothermic reduction of ceria. The conservation equations for solid and fluid phases are coupled by the source term $Q_{\text{sf}} = -Q_{\text{fs}} = h_{\text{fs}} \cdot A_{\text{fs}} (T_f - T_s)$, where $h_{\text{fs}}$ is the interfacial heat transfer coefficient, $A_{\text{fs}}$ is the fluid-solid area density, and $T_s$ and $T_f$ are the temperatures of the solid and the fluid, respectively. An artificially high $h_{\text{fs}}$ of 10’000 W m$^{-1}$ K$^{-1}$ enforces thermal equilibrium between the two phases ($T_s = T_f$). This is reasonable due to the assumption of the fluid being stationary. According to the correlation described in reference [107], $A_{\text{fs}}$ is set to 951.8 m$^{-1}$.

For the fluid phase of the RPC domain, the energy conservation equation is given by

$$
\frac{\partial}{\partial t} (\phi_{\text{dual}} \rho h) = \nabla \cdot (k \nabla T) + S_{\text{radiation}} + Q_{\text{fs}}
$$

(3.3)

where $S_{\text{radiation}}$ is the source term accounting for radiation exchange. Due to a constraint in ANSYS CFX that only allows radiative heat transfer in the fluid and not in the solid phase of porous domains, the radiative properties of the fluid are set to the effective radiative properties of the RPC; local thermal equilibrium between the fluid and the solid phase is enforced. The radiative transfer equation for the RPC, modelled as an isotropic, gray, absorbing-emitting-scattering participating media, is

$$
\frac{dI(\bar{r}, \bar{s})}{ds} = -\beta I(\bar{r}, \bar{s}) + \alpha I_b(\bar{r}) + \frac{\sigma}{4\pi} \int_{4\pi} I(\bar{r}, \bar{s}') d\omega'
$$

(3.4)

where $\bar{r}$ is the position vector, $\bar{s}$ is the direction vector, $s$ is the path length, $\beta$, $\alpha$ and $\sigma$ are the extinction, absorption and scattering coefficients, respectively, $I$ is the radiation intensity, $I_b$ is the blackbody radiation intensity depending on the
local temperature, and $\omega$ is the solid angle. For the geometric optics regime, $\alpha = \beta \cdot (1 - r)$ and $\sigma = \beta \cdot r$, where $r$ is the reflectivity of CeO$_2$. The radiation exchange source term in equation (3.3) is calculated as

$$S_{\text{radiation}} = \alpha \left( 4\pi I_b - \int_{4\pi} I d\omega \right)$$

which accounts for emission and absorption inside the porous RPC structure.

### 3.2.2 Boundary conditions and source terms

The boundary conditions and source terms are schematically indicated in Figure 3.1. At the outer surface of the insulating jacket, the exposed surface of the reactor shell not covered by the jacket, and the lateral surface of the aluminum front, energy is lost by radiative and convective heat transfer. The convective heat transfer coefficient is conservatively assumed to be 15 W m$^{-1}$ K$^{-1}$. Due to moderate surface temperatures, the temperature distribution within the solar reactor is insensitive to the value of heat transfer coefficient taken on these surfaces. The ambient air temperature, water cooling channel temperature, and the quartz window temperature are all assumed to be at 293 K. The front surface of the aluminum front of the reactor is assumed to be adiabatic. The mean transmissivity of the 12 mm thick quartz window was experimentally measured to be $\tau = 0.929$. Flux maps were acquired by a calibrated CCD camera viewing a Lambertian target while it was irradiated with the HFSS. The 300 mm diameter quartz window was placed in front of the target such that it could intercept the entire light cone produced by the HFSS. By comparing flux maps taken with and without the window intercepting the radiation, the mean transmissivity, thereby averaged over all incident angles of the radiation, could be extracted. The volumetric and surface heat sources $S_{\text{solar}}$ within the RPC and on the front insulation surface were derived using a decoupled Monte Carlo (MC) ray tracing model. This model yields the absorbed radiative power delivered by the HFSS. For the calculation of the nonstoichiometry $\delta$ of ceria, thermodynamic equilibrium is assumed, as previous experimental work with similar ceria RPCs has shown that the reduction step is heat transfer limited [50]. The oxygen partial pressure is assumed to be constant at $p_{O_2} = 5$ mbar due to operation under
vacuum. The energy sink $S_{\text{reaction}}$, accounting for the endothermic reduction reaction, is calculated using the two expressions for equilibrium $\delta$ [63] and reaction enthalpy $\Delta H_{O_2}$ [88], listed in Table 3.1.

### 3.2.3 Material properties

Material properties of the ceria RPC with dual-scale porosity are listed in Table 3.1. The dual-scale porosity of the RPC was calculated by measuring its mass and volume. The strut porosity was assessed with a combination of mercury intrusion porosimetry (Quantachrome Poremaster 60-GT) and geometric approximations to calculate the size of the hollow struts. The value for the number of pores per inch was provided by the manufacturer of the polyurethane foams used to manufacture the RPCs. The effective heat and mass transfer properties of the RPC structure were taken from literature. The correlation for the total hemispherical reflectance of $\text{CeO}_2$ was evaluated for an average reduction state of $\delta = 0.035$ and depends on the local temperature in the heat transfer model. To calculate the heat source $S_{\text{solar}}$ using the MC ray tracing model, a correlation weighted according to Planck’s law for blackbody temperatures of 5780 K, which is a good approximation of solar radiation, was used, resulting in $r = 0.2905$ [109]. For the calculation of the effective thermal conductivity of the RPC, thermal conductivity of the fluid was set to zero, due to operation under vacuum.

The heat transfer properties of the solid domains are listed in Table 3.2. They were either taken from literature, or values from the manufacturers were used. For the specific heat capacity of the $\text{Al}_2\text{O}_3$−$\text{SiO}_2$ insulation, a mass-weighted average of alumina and silica heat capacities was calculated according to the chemical composition, as suggested in reference [110]. Fluid domain properties were taken as a modified inert gas for simplicity, as the domain has negligible contribution to heat transfer.
Table 3.1. Morphological and effective heat transfer properties of the ceria RPC.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Correlation</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dual-scale porosity</td>
<td>$\phi_{\text{dual}} = 0.78$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strut porosity</td>
<td>$\phi_{\text{strut}} = 0.3561$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-scale porosity</td>
<td>$\phi_{\text{single}} = \frac{\phi_{\text{dual}} - \phi_{\text{strut}}}{1 - \phi_{\text{strut}}} = 0.6583$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of pores per inch</td>
<td>$n_{\text{ppi}} = 10$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>$d_m = (5.302 \cdot 10^{-5} \cdot \phi_{\text{single}} + 2.155 \cdot 10^{-5}) \cdot \frac{357}{n_{\text{ppi}}} = 2.015 \cdot 10^{-3}$ m</td>
<td></td>
<td>[107]</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>$\beta = \frac{-630.674 \cdot \phi_{\text{single}}^2 - 120.06 \cdot \phi_{\text{single}} + 1229.36}{1000 \cdot d_m} = 435.15$ m$^{-1}$</td>
<td></td>
<td>[107]</td>
</tr>
<tr>
<td>Total hemispherical reflectance (at $\delta = 0.035$)</td>
<td>$r = 0.41184 - 2.419 \cdot 10^{-5} \cdot T$</td>
<td></td>
<td>[109]</td>
</tr>
<tr>
<td>Density CeO$_2$</td>
<td>$\rho_{\text{CeO}_2} = 7220$ kg m$^{-3}$</td>
<td></td>
<td>[65]</td>
</tr>
<tr>
<td>Molar mass</td>
<td>$M_{\text{CeO}_2} = 0.1721$ kg mol$^{-1}$</td>
<td></td>
<td>[111]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>$c_{p,\text{CeO}<em>2} = \frac{67.95 - 9.9 \cdot 10^5 \cdot T^{-2} + 0.0125 \cdot T}{M</em>{\text{CeO}_2}}$ J kg$^{-1}$ K$^{-1}$</td>
<td></td>
<td>[112]</td>
</tr>
<tr>
<td>Thermal conductivity CeO$_2$</td>
<td>$k_{\text{CeO}_2} = -1.723 \cdot 10^{-9} \cdot T^3 + 1.12 \cdot 10^{-8} \cdot T^2 - 0.024 \cdot T + 17.8$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td>[113]</td>
</tr>
<tr>
<td>Effective thermal conductivity</td>
<td>$k_{\text{eff}} = k_{\text{CeO}<em>2} \cdot (1 - 0.6223 \cdot \phi</em>{\text{dual}}) \cdot (1 - 1.055 \cdot \phi_{\text{dual}})$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td>[114]</td>
</tr>
<tr>
<td>Equilibrium thermodynamics ($T$ in °C)</td>
<td>$\delta = 10^{-2.15 \cdot 10^{-6} \cdot T^2 - 0.88 \cdot 10^{-3} \cdot T + 12.2} \cdot \left(\frac{P_{O_2}}{P_0}\right)^{1.25 \cdot 10^{-7} \cdot T^2 - 3.1 \cdot 10^{-4} \cdot T - 1.83 \cdot 10^{-2}}$</td>
<td></td>
<td>[107]</td>
</tr>
<tr>
<td>Reaction enthalpy</td>
<td>$\Delta H_{\text{O}_2} = 969.409 - 503.739 \cdot \delta^{0.5}$ kJ mol$^{-1}$</td>
<td></td>
<td>[88]</td>
</tr>
</tbody>
</table>
Table 3.2. Material properties of the reactor components.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Correlation</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al₂O₃-SiO₂ insulation (Rath, Inc. KVS184/400)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>( \rho_{\text{ins}} = 400 )</td>
<td>kg m(^{-3})</td>
<td>[115]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>( c_{p,\text{ins}} = -3.09 \cdot 10^{-10} \cdot T^4 + 1.71 \cdot 10^{-6} \cdot T^3 - 3.48 \cdot 10^{-3} \cdot T^2 + 3.18 \cdot T + 101 )</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>[116, 117]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( k_{\text{ins}} = -2.09 \cdot 10^{-11} \cdot T^3 + 1.06 \cdot 10^{-7} \cdot T^2 + 3.69 \cdot 10^{-5} \cdot T + 7.07 \cdot 10^{-2} )</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>[115]</td>
</tr>
<tr>
<td>Hemispherical total emittance</td>
<td>( \varepsilon_{\text{ins}} = 0.28 )</td>
<td></td>
<td>[118]</td>
</tr>
<tr>
<td><strong>Stainless steel 316L shell</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>( \rho_{\text{shell}} = 8000 )</td>
<td>kg m(^{-3})</td>
<td>[119]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>( c_{p,\text{shell}} = 412 + 0.2 \cdot T - 2 \cdot 10^{-5} \cdot T^2 )</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>[120]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( k_{\text{shell}} = 0.013 \cdot T + 11.45 )</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>[119]</td>
</tr>
<tr>
<td>Hemispherical total emittance</td>
<td>( \varepsilon_{\text{shell}} = 0.57 )</td>
<td></td>
<td>[121]</td>
</tr>
<tr>
<td><strong>Insulating jacket</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>( \rho_{\text{jacket}} = 80 )</td>
<td>kg m(^{-3})</td>
<td>[122]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>( c_{p,\text{jacket}} = 840 )</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>[122]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( k_{\text{jacket}} = 5.319 \cdot 10^{-7} \cdot T^2 - 2.487 \cdot 10^{-4} \cdot T + 6.433 \cdot 10^{-2} )</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>[122]</td>
</tr>
<tr>
<td>Hemispherical total emittance</td>
<td>( \varepsilon_{\text{jacket}} = 0.89 )</td>
<td></td>
<td>[123]</td>
</tr>
<tr>
<td><strong>Aluminum front</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>( \rho_{\text{Al}} = 2700 )</td>
<td>kg m(^{-3})</td>
<td>[124]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>( c_{p,\text{Al}} = 706.7 + 0.6 \cdot T - 1 \cdot 10^{-4} \cdot T^2 )</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>[120, 125]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( k_{\text{Al}} = -4.01 \cdot 10^{-10} \cdot T^4 + 1.14 \cdot 10^{-6} \cdot T^3 - 1.22 \cdot 10^{-3} \cdot T^2 + 0.53 \cdot T + 162 )</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>[110, 126]</td>
</tr>
<tr>
<td>Hemispherical total emittance</td>
<td>( \varepsilon_{\text{Al}} = 0.09 )</td>
<td></td>
<td>[121]</td>
</tr>
</tbody>
</table>
3.2.4 Initial condition

To establish the initial condition, the solar reactor was heated from room temperature for one hour with a radiative power input, evaluated at the reactor window, of $P_{\text{solar}} = 10$ kW. Subsequently, $P_{\text{solar}}$ was set to zero, and the reactor was allowed to cool naturally to the desired start temperature. The temperature field established with the preheating simulation was then applied as an initial condition for the transient reduction simulation and all subsequent analysis. It was confirmed experimentally that the initial condition is accurate, and further established that small variations in the initial condition (temperature field) do not have a significant influence on the final temperature field after reduction.

3.2.5 Numerical solution

The heat sources $S_{\text{solar}}$ were calculated by applying an in-house MC ray tracing code [127] with $10^9$ rays. The heat transfer simulations were performed with ANSYS CFX (version 17.0). To discretize the governing equations in space, between 35’115 and 54’980 hexahedral cell elements were used. Due to a limitation in ANSYS CFX, a single cell had to be extruded in the third direction around the symmetry axis. For the discretization in time, a constant time step of 1 s was used. The finite volume method was applied with a second-order backward Euler scheme. To solve the radiative transfer equation (equation (3.4)), the discrete transfer model was used, transforming the equation into a set of transport equations for $I$ and solving for discrete solid angles along $s$. The simulations were performed using the high-performance cluster Euler of ETH Zurich.
3.3 Experimental validation

The heat transfer model was validated by comparing the calculated temperature and oxygen evolution to the experimentally determined values measured during testing of the solar reactor in the HFSS. RPC cavity #1 (see Table 2.1 for specifications) was simulated at a radiative solar power input of $P_{\text{solar}} = 30.5$ kW. The corresponding experimental values are summarized in Table 2.2 in section 2.2 of the previous chapter\(^1\). Figure 3.2 (a) shows the numerically calculated (solid lines) and the experimentally measured (dashed lines) temperatures at the different thermocouple positions as indicated in Figure 3.1. The agreement between simulation and experiment is reasonably good for all thermocouple positions, most importantly the B-type thermocouples in contact with the back of the RPC (standard deviation between experimental and numerical $T_{\text{RPC,nom}}$ during reduction was 9.4 °C). For both the simulation and the experiment, the RPC temperature at the front position ($T_{B,3}$) is significantly lower than the temperatures towards the back of the RPC ($T_{B,1}$ and $T_{B,2}$). The temperature of the Al$_2$O$_3$–SiO$_2$ insulation at the innermost position ($T_{K,1}$) is slightly overestimated in the simulation. This is because the thermal conductivity of the porous insulation is assumed constant, whereas in reality it changes between the reduction step, which is operated under vacuum, and the oxidation step, which is operated at atmospheric pressure. Temperatures of the reactor shell ($T_{K,4}$) and the insulating jacket ($T_{K,5}$) are slightly underestimated in the simulation, due to a lower initial condition for the external surfaces, however, the curvature still matches experimental results. In Figure 3.2 (b), $T_{\text{RPC,nom}}$ and the O$_2$ release rate are shown for the simulation (solid lines) and the experiment (dashed lines). The two curves for $T_{\text{RPC,nom}}$ match well, with the maximum temperature being 1470 °C for the simulation and 1489 °C for the experiment. The O$_2$ release at low temperatures is slightly overestimated in the simulation, however, the integrated value of 31.1 L matches well with the experimentally measured integrated amount of 30.1±0.6 L (4% difference).

\(^1\) Due to the two-dimensional axisymmetric solar reactor model, the nominal RPC temperature $T_{\text{RPC,nom}}$ is defined in this chapter as the average of three measurement points, compared to four measurement points in chapter 2. As a result, the values reported here for $T_{\text{RPC,nom}}$ differ slightly from the corresponding values reported in the previous chapter.
Figure 3.2. (a) Numerically calculated (solid lines) and experimentally measured (dashed lines) temperatures at the locations indicated in Figure 3.1, during the reduction step and the subsequent natural cooling phase. (b) Average of the three thermocouple locations measuring the temperature of the RPC at the back surface ($T_{RPC,nom}$) and O$_2$ evolution as a function of time.
The solar-to-fuel energy conversion efficiency is defined as

\[
\eta_{\text{solar-to-fuel}} = \frac{Q_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{pump}} + Q_{\text{inert}}}
\]  

(3.6)

Because the oxidation reaction is not included in the solar reactor model, but complete re-oxidation using CO₂ is assumed, the energy content of the fuel (CO) produced is calculated as \( Q_{\text{fuel}} = \Delta H_{\text{fuel}} \cdot 2 \int r_{O_2} \, dt \), where \( \Delta H_{\text{fuel}} \) is the heating value of CO (\( \Delta H_{\text{CO}} = 283 \, \text{kJ mol}^{-1} \)) and \( \int r_{O_2} \, dt \) is the rate of released O₂ integrated over the reduction step. \( Q_{\text{solar}} \) is the total solar energy input integrated over the reduction step. \( Q_{\text{pump}} \) and \( Q_{\text{inert}} \) are the energy penalties associated with vacuum pumping and the consumption of the inert gas Ar during the reduction step, respectively, and are calculated as suggested in reference [53] and described in section 2.1.4 of the previous chapter. An efficiency of \( \eta_{\text{solar-to-fuel}} = 3.38\% \) was predicted by the simulation, which is comparable to the experimentally determined efficiency \( \eta_{\text{solar-to-fuel}} = 3.26 \pm 0.07\% \). Heat recovery was not applied. The slight overestimation is correlated directly to the slight overestimation in total O₂ yield from the simulation.

### 3.4 Modelling results and discussion

The validated numerical model is a useful tool not only to better understand the performance of the current solar reactor, but also to assess the influence of various design and operational changes on the performance of the reactor. In the subsequent analysis, a base case simulation representing the experimental validation case (as described in section 3.3) is used to perform a parametric study of several crucial design variables of the ceria RPC. The critical parameters of the base case simulation are summarized in Table 3.3.

#### 3.4.1 Incident solar radiation and temperature distribution

A contour plot of absorbed incoming solar radiation from the HFSS, \( S_{\text{solar}} \), is shown in Figure 3.3 (a). \( S_{\text{solar}} \) is constant during the reduction step. Due to the relatively large optical thickness of the RPC (\( \tau_{\text{RPC}} = \beta \cdot t_{\text{RPC}} = 10.9 \)), more than 90% of the incoming radiation is absorbed within the first five millimeters of the RPC structure, which can clearly be seen in the figure. Due to the uneven
distribution of the incoming solar radiation, caused by the discrete nature of the HFSS radiation source, $S_{\text{solar}}$ is high towards the back corner of the RPC structure and relatively low at the center of the back. Figure 3.3 (b) shows the temperature distribution within the solid and the RPC domain of the reactor at the end of the reduction step, and of the RPC domain only (enlarged). The hottest regions in the temperature profile within the RPC correspond to the areas of highest $S_{\text{solar}}$; the front, directly irradiated surface of the RPC reaches the highest temperatures, while the back of the RPC and areas which are less directly irradiated remain at lower temperatures. This non-uniformity of temperature within the RPC limits the efficiency that can be achieved with the solar reactor, as the nonstoichiometry $\delta$ (a measure of oxygen released during reduction) is directly correlated to the ceria temperature which is achieved. To achieve a more uniform temperature distribution using highly concentrated sunlight, and do so quickly enough to reach a high solar-to-fuel energy conversion efficiency, the macroporosity (millimeter-scale) of the absorber material (in this case an RPC) must be substantially increased.

Table 3.3. RPC and operational parameters of the base case simulation. These values correspond to the parameters of the validation experiment.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RPC morphology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dual-scale porosity</td>
<td>$\phi_{\text{dual}} = 0.78$</td>
<td></td>
</tr>
<tr>
<td>Number of pores per inch</td>
<td>$n_{\text{ppi}} = 10$</td>
<td></td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>$\beta = 435.15$</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>Thickness of RPC</td>
<td>$t_{\text{RPC}} = 25$</td>
<td>mm</td>
</tr>
<tr>
<td>Ceria mass loading</td>
<td>$m_{\text{RPC}} = 18.38$</td>
<td>kg</td>
</tr>
<tr>
<td><strong>Operational parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar radiative power input</td>
<td>$P_{\text{solar}} = 30.5$</td>
<td>kW</td>
</tr>
<tr>
<td>Partial pressure of oxygen</td>
<td>$P_{O_2} = 5$</td>
<td>mbar</td>
</tr>
<tr>
<td>Reduction start temperature</td>
<td>$T_{\text{red,start}} = 730$</td>
<td>°C</td>
</tr>
<tr>
<td>Reduction end temperature</td>
<td>$T_{\text{red,end}} = 1466$</td>
<td>°C</td>
</tr>
</tbody>
</table>
Figure 3.3. (a) Distribution of $S_{\text{solar}}$ within the ceria RPC during the reduction step. (b) Temperature distribution of the solid domains, and of the RPC domain (also enlarged) at the end of the reduction step. Also indicated is the variable $x$, which defines the cross-section position through the RPC for the evaluation of absorbed solar radiation and temperature (analyzed in Figure 3.8).
3.4.2 Energy flows

The instantaneous energy balance for the reduction step is illustrated as a function of time in Figure 3.4 for the base case at $P_{\text{solar}} = 30.5$ kW. Note that heat recovery was not applied. Losses by reradiation from the hot cavity, the change in sensible heat content of the RPC, the remaining reactor components ($\text{Al}_2\text{O}_3-\text{SiO}_2$ insulation, aluminum front, reactor shell, and insulating jacket), the energy consumed by the endothermic reduction reaction, the conductive heat loss to the water-cooled reactor front, and other heat losses are indicated. Other heat losses include reflection of incoming solar radiation inside the reactor cavity and at the quartz window, absorption of incoming radiation at the window, and convection and radiation at the outer reactor surfaces. Initially, sensible heating of the RPC dominates energy consumption, consuming 87% of $P_{\text{solar}}$, while on average it consumes 33%. By the end of the reduction step, reradiation dominates heat loss, accounting for 31% of $P_{\text{solar}}$ on average and 45% at the peak. Reradiation losses could be lowered by decreasing the size of the aperture, provided that solar radiation can be delivered with higher concentration. A selective coating with high transmissivity in the visible region of the solar spectrum, but high reflectivity in the IR region of the radiation emitted by the hot cavity, could be considered for the quartz window, provided that the coating can withstand very high temperatures (>500 °C). Reradiation losses also decrease with increasing power input $P_{\text{solar}}$ because the ceria remains at high temperatures for less time when the reduction duration shortens. Sensible heating of the bulk materials consumes 21% of $P_{\text{solar}}$ on average, but levels off early in the reduction cycle, with the $\text{Al}_2\text{O}_3-\text{SiO}_2$ insulation being the dominant consumer, while the aluminum front, reactor shell, and insulating jacket consume 1.2% or less each. Energy loss through sensible heating of the bulk materials could be lowered if insulation materials with lower specific heat capacity were used. The energy fraction driving the endothermic reduction reaction of ceria quickly increases with time, and on average accounts for 5.6% of $P_{\text{solar}}$. The conduction heat losses to the water-cooled reactor front are significant, with an average consumption of 2.7% of $P_{\text{solar}}$. The losses by convection and radiation at the outer reactor surfaces, as well as the energy lost by reflection of the incoming solar radiation inside the reactor cavity, account for less than 0.3% of $P_{\text{solar}}$ each. The remaining
7.1% of $P_{\text{solar}}$ is lost by absorption and reflection at the quartz window ($\tau = 0.929$). Although not considered in the simulation, convective losses associated with gasses exiting the solar reactor during the reduction step are also negligible (less than 0.3% of the input power). The share of energy used to drive the reduction reaction, and therefore also representative of the solar-to-fuel energy conversion efficiency, could potentially be increased by using doped ceria to increase the reduction extent [55, 56], or by minimizing the temperature swing with near isothermal operation [79, 128, 129], although this does not necessarily increase the efficiency due to other limitations introduced with a lower temperature swing.

![Energy balance diagram](image)

**Figure 3.4.** Instantaneous energy balance for the duration of a reduction step. Other heat losses include convection and radiation at the outer reactor surfaces, reflection of incoming solar radiation inside the reactor cavity, and absorption and reflection at the quartz window.

### 3.4.3 Parameter study

Operational and design parameters of the solar reactor can be optimized using the numerical model. The most critical parameters are the level of input power and the structure of the ceria RPC. These two parameters are coupled, as higher power is only beneficial if it can be more uniformly absorbed within the RPC.
structure. If solar radiation is only absorbed within the first small fraction of RPC depth, performance becomes limited by the maximum sustainable surface temperature of the ceria RPC. A parametric study was conducted using the parameters listed in Table 3.3 as the base case. The following parameters were varied in the study: RPC thickness $t_{\text{RPC}}$, RPC dual-scale porosity $\phi_{\text{dual}}$, and the radiative power input $P_{\text{solar}}$. All of the simulations were initialized with $T_{\text{RPC,nom}} = 730$ °C, and the duration of the reduction step $t_{\text{red}}$ was controlled by setting $P_{\text{solar}}$ to zero once $T_{\text{RPC,nom}} = 1466$ °C was reached. The results of the parameter study are shown in Figure 3.5–Figure 3.7. For each case, the nominal RPC temperature $T_{\text{RPC,nom}}$ and the oxygen release rate are plotted as a function of time in (a). In (b), the variable parameters are plotted versus $\eta_{\text{solar-to-fuel}}$, $t_{\text{red}}$, the reduction time required to reach $T_{\text{RPC,nom}} = 1466$ °C, and $T_{\text{RPC,max}}$, the maximum temperature of the RPC reached at the end of the reduction step, which is a critical value for the mechanical stability of the RPCs.

**RPC thickness $t_{\text{RPC}}$** – The effect of changing RPC thickness $t_{\text{RPC}}$ is shown in Figure 3.5. The inner, directly irradiated surface area of the RPC as well as the thickness of the separating gap between the RPC and the Al$_2$O$_3$–SiO$_2$ insulation were kept constant, while the thickness of the insulation was adapted slightly (and with negligible effect). For both higher and lower $t_{\text{RPC}}$ values compared to the base case, $\eta_{\text{solar-to-fuel}}$ slightly decreases, while $t_{\text{red}}$ increases with increasing RPC thickness. This is due to the increasing ceria mass loading of the reactor, and consequently longer duration of the reduction step, which yields a higher total amount of O$_2$ released. This can be seen in Figure 3.5 (a). Due to the increased thickness of the RPC, $T_{\text{RPC,max}}$ increases as the end of the reduction step is controlled by the temperature at the back surface of the RPC. It is important to note the scale of the efficiency metric, which shows that large variation in the RPC thickness parameter, while yielding a trend, only impacts the efficiency by a fraction of a percent.
Figure 3.5. (a) Nominal RPC temperature $T_{\text{RPC,nom}}$ and O$_2$ release rate as a function of time for varying RPC thickness $t_{\text{RPC}}$. (b) Efficiency $\eta_{\text{solar-to-fuel}}$, reduction time $t_{\text{red}}$ and maximum RPC temperature $T_{\text{RPC,max}}$ of these cycles as a function of $t_{\text{RPC}}$. 
RPC porosity $\phi_{\text{dual}}$ – The effect of changing RPC porosity $\phi_{\text{dual}}$ is illustrated in Figure 3.6. The only variable adjusted is $\phi_{\text{dual}}$, while $\phi_{\text{single}}$ and $n_{\text{ppi}}$ are kept constant. The chosen values of $\phi_{\text{dual}}$ correspond to a change in ceria mass loading of $\pm 25\%$ compared to the base case. $\eta_{\text{solar-to-fuel}}$ decreases slightly from $3.54\%$ at $\phi_{\text{dual}} = 0.725$ to $3.14\%$ at $\phi_{\text{dual}} = 0.835$. The influence on $t_{\text{red}}$ is higher, with a decrease from $16.1 \text{ min ($}\phi_{\text{dual}} = 0.725\text{ )}$ to $9.15 \text{ min ($}\phi_{\text{dual}} = 0.835\text{ )}$, mainly caused by the significant difference in ceria mass loading. Similar to the impact of changing RPC thickness, the effect of decreasing reduction time is counteracted by a decrease in total O$_2$ released, and therefore the efficiency only changes slightly. With increasing $\phi_{\text{dual}}$, the optical thickness of the RPC decreases, leading to a slightly lower $T_{\text{RPC, max}}$.

Solar radiative power input $P_{\text{solar}}$ – The most influential variable is the solar radiative power input, as can be seen in Figure 3.7. Increasing $P_{\text{solar}}$ drastically decreases $t_{\text{red}}$ and increases the efficiency $\eta_{\text{solar-to-fuel}}$. Roughly doubling $P_{\text{solar}}$ from 30.5 kW to 60 kW cuts $t_{\text{red}}$ by more than half (12.3 min to 5.0 min) and more than doubles $\eta_{\text{solar-to-fuel}}$ (from 3.38\% to 7.34\%). This is attributed primarily to two phenomena: first, heat losses, especially by reradiation, decrease due to a shorter reduction time, and second, higher RPC temperatures towards the irradiated front surface directly lead to higher oxygen nonstoichiometry $\delta$. $T_{\text{RPC, max}}$ increases from 1719 °C at $P_{\text{solar}} = 30.5$ kW to 1914 °C at $P_{\text{solar}} = 60$ kW.
Figure 3.6. (a) Nominal RPC temperature $T_{\text{RPC,nom}}$ and O$_2$ release rate as a function of time for varying RPC porosity $\phi_{\text{dual}}$. (b) Efficiency $\eta_{\text{solar-to-fuel}}$, reduction time $t_{\text{red}}$ and maximum RPC temperature $T_{\text{RPC,max}}$ of these cycles as a function of $\phi_{\text{dual}}$. 
Figure 3.7. (a) Nominal RPC temperature $T_{\text{RPC, nom}}$ and O$_2$ release rate as a function of time for varying input power $P_{\text{solar}}$. (b) Efficiency $\eta_{\text{solar-to-fuel}}$, reduction time $t_{\text{red}}$ and maximum RPC temperature $T_{\text{RPC, max}}$ of these cycles as a function of $P_{\text{solar}}$. 

[Diagram showing temperature and efficiency changes with power input]
3.4.4 Advanced reactor design

An additional case was considered to assess the possibility of designing a solar receiver-reactor with parameters optimized beyond the current means of production. This advanced reactor design features much larger pores ($n_{\text{ppi}} = 3$; average macropore diameter $\approx 7$ mm) to dramatically enhance volumetric absorption, but the same porosity and thereby mass loading as in the base case. In Figure 3.8 (a), the absorbed solar radiation $S_{\text{solar}}$ as well as the local RPC temperature are shown as a function of the penetration depth for the advanced RPC design. The location of extraction of these variables is indicated in Figure 3.3. For comparison, the results for the case with $n_{\text{ppi}} = 10$ (average macropore diameter $\approx 2$ mm) are also shown. In both cases, $P_{\text{solar}}$ was set to 60 kW and the values correspond to a simulation time of 298 s, which is the time when the reduction step ends in the case of $n_{\text{ppi}} = 10$. In the case of $n_{\text{ppi}} = 3$, $S_{\text{solar}}$ is more uniformly distributed, leading to a more uniform distribution of temperature within the RPC. The temperature difference between the front and the back of the RPC equals 113 °C, compared to 377 °C for $n_{\text{ppi}} = 10$. The more uniform distribution of temperature within the RPC directly results in higher performance of the solar reactor when it is properly operated. Due to the lower temperature difference between the front and the back of the RPC, $t_{\text{red}}$ can be extended without exceeding the critical value for the maximum RPC temperature. This is illustrated in Figure 3.8 (b), which shows the nominal RPC temperature and the rate of released oxygen as a function of time for $n_{\text{ppi}} = 3$ (solid lines) and for $n_{\text{ppi}} = 10$ (dashed lines). For $n_{\text{ppi}} = 3$, $t_{\text{red}}$ is extended to 423 s. Due to the more uniform temperature distribution, this results in the same critical value of $T_{\text{RPC,max}} = 1914$ °C at the end of the reduction step as in the case of $n_{\text{ppi}} = 10$. As a consequence, the total amount of $O_2$ released drastically increases from 53.55 L ($n_{\text{ppi}} = 10$) to 106.5 L ($n_{\text{ppi}} = 3$), which ultimately results in a better performance of the solar reactor ($\eta_{\text{solar-to-fuel}} = 10.2\%$ compared to $\eta_{\text{solar-to-fuel}} = 7.34\%$ for $n_{\text{ppi}} = 10$). However, the path to realizing a ceria structure with the physical parameters required to obtain this level of performance is ongoing research and development [95, 96]. Note that this analysis does not consider heat recovery.
Figure 3.8. (a) Absorbed solar radiation $S_{\text{solar}}$ and RPC temperature as a function of $x$, the depth within the RPC, where zero indicates the front, directly irradiated surface. The position of evaluation within the RPC is indicated in Figure 3.3. Values are extracted for a simulation time of 298 s, corresponding to $t_{\text{red}}$ of the case with $n_{\text{ppi}} = 10$. (b) Nominal RPC temperature $T_{\text{RPC,nom}}$ and rate of released $O_2$ as a function of time. Solid lines represent the advanced RPC design with $n_{\text{ppi}} = 3$ and dashed lines represent the case with $n_{\text{ppi}} = 10$. For both cases, $P_{\text{solar}}$ was set to 60 kW.
It is important to consider the impact of volumetric absorption and uniform heating when analyzing and scaling solar reactors. With typical chemical reactors, for example continuously stirred thermal reactors, scaling up results in significantly increased thermal performance because of the increased ratio of active volume to external surface area [130]. For solar RPC reactor technology, however, this is not the case because the active volume is limited to the ceria RPC. The solar reactor analyzed in this study is more than 12 times larger than its precursor technology, where an efficiency of 5.25% was experimentally demonstrated [53], and yet an efficiency of only 6.12% is predicted here for the nominal 50 kW case and otherwise similar operating conditions. This is directly due to a decreasing active volume fraction which results from scaling an RPC solar reactor; at the 4 kW scale, the ceria RPC represented 60% of the chemical reactor volume, while at the 50 kW scale it is only 30%. Assuming a constant apparent mass density inside the ceria RPC, the total mass loading of the reactor is limited in the same way. In 2012 Furler et al. [50] determined that ceria RPCs outperformed ceria blocks and felts because of the structure’s relatively enhanced radiation heat transfer properties, although direct absorption of solar radiation was still limited. In the present study, it became clear that for solar reactors of this type to operate efficiently, increased utilization of the cavity volume by achieving higher volumetric absorption of the incoming solar radiation, and thus volumetric heating, is necessary.

The impact that sensible heat recovery could have on the performance of a solar reactor is evident from the energy balance presented in Figure 3.4. Previous studies have considered various forms of heat recovery and the implication on both reactor and system level efficiency [83, 89, 100, 128]. For the reactor technology discussed here, consisting of stationary redox ceramics which are directly irradiated in temperature and pressure swing operation, heat recovery options are limited. The possibility to actively recover heat during the cooling step after reduction exists, but its impact is limited by the need to utilize an inert gas heat transfer fluid for multiple stages of solid-gas heat exchange [91].

A simple energy balance analysis can be performed to determine the impact of extracting heat from the stationary ceria mass between the reduction and
oxidation steps and providing it back to the solar reactor. Considering the case of 50 kW of solar input power for the base RPC parameters listed in **Table 3.3** (total ceria mass of 18.4 kg covering 30% of the reactor volume), a solar-to-fuel energy conversion efficiency of 6.12% was determined. 7,813 kJ of energy is contained as sensible heat in the ceria solid (42% of the solar energy input during the reduction step). For the purpose of discussing the potential of minimizing this irreversibility, 100% of this sensible heat is considered to be recoverable. Accounting for this recoverable heat as a subtraction from the denominator of equation (3.6), presumably representing the fact that less solar energy would be required to heat the solid, and further accounting for less energy lost by reradiation because of the resulting shorter reduction time (212 s versus 368 s), an efficiency of $\eta_{\text{solar-to-fuel}} = 12.75\%$ is determined. It is important to note that removing and reusing even 50% of the sensible heat contained in the ceria RPC represents a major engineering challenge.
3.5 Summary and conclusions

The development and use of an experimentally validated transient heat transfer model of the ceria RPC solar reactor designed for pressure and temperature swing thermochemical redox cycling has been reported. The performance of the solar reactor was analyzed using the model by considering, among other metrics, the solar-to-fuel energy conversion efficiency. The numerical results indicate the prominent influence of solar radiative input power, and therefore the solar concentration ratio at the aperture, where increasing power substantially reduces reduction time. For $P_{\text{solar}} = 50$ kW, the model predicts $\eta_{\text{solar-to-fuel}} = 6.12\%$. For this case, if 100% of the sensible heat is recovered from the ceria RPC mass between reduction and oxidation steps, the cycle efficiency can be increased to 12.75%. Further measures to boost $\eta_{\text{solar-to-fuel}}$ include increasing the millimeter-scale porosity of the RPC structure to allow for more volumetric absorption of incoming solar radiation, resulting in a more uniform temperature distribution within the RPC, which ultimately improves the performance of the solar reactor. For example, an increase in macropore diameter from roughly 2 mm to 7 mm ($n_{\text{ppi}}$ 10 to 3) resulted in an increase of $\eta_{\text{solar-to-fuel}}$ from 7.34% to 10.2%. If volumetric absorption and uniform heating is achieved inside the ceria RPC, mass loading could also be increased to obtain higher efficiencies, provided the latter criteria of uniform heating is not compromised in the process. While the numerical model indicates the potential of this solar receiver-reactor technology to achieve high efficiency, critical issues remain: (i) stable ceria structures with optimized volumetric absorption characteristics (i.e., ordered structures) must be fabricated and demonstrated to survive in the solar reactor environment, and (ii) with increased power, the directly irradiated surface area of the redox active material will always be at risk of sublimation; the search for new redox active materials which can be reduced at lower temperatures while maintaining favorable oxidation properties is critically important [56, 57, 131].
4 On-sun demonstration of CO$_2$ and H$_2$O splitting$^1$

In this chapter, the experimental facility for on-sun testing of the solar reactor is described and experimental results for CO$_2$ and H$_2$O splitting are presented. The experimental facility features three main subsystems: a high-flux solar concentrating heliostat field and tower, the solar thermochemical reactor system including a dedicated power measurement system, and a gas-to-liquid conversion plant to process the syngas produced in the solar reactor to liquid hydrocarbon fuels on-site via Fischer-Tropsch synthesis. The solar reactor contains a ceria RPC cavity that is optimized for the operation in the solar tower. It features an adapted geometry designed to prevent structural failure when the reactor is in operation in the solar tower, tilted by 40 degrees towards the heliostat field, and adjusted RPC properties for maximum performance.

With the adapted solar reactor, a maximum solar-to-fuel energy conversion efficiency of 5.6±1.0% is experimentally demonstrated for CO$_2$ splitting. For the co-splitting of H$_2$O and CO$_2$, different possibilities to control the composition of the produced syngas are presented. With operating conditions that result in a syngas composition suitable for Fischer-Tropsch processing, 62 consecutive redox cycles are performed with the same ceria RPC cavity. The produced syngas is collected and stored to further process it on-site to liquid hydrocarbon fuels.

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4.1 Experimental setup and methods

4.1.1 Solar reactor design

The solar reactor design was described in detail in section 2.1.1. For the operation in the solar tower in Spain, a few specifications had to be adjusted. The reactor configuration installed in the solar tower is schematically shown in Figure 4.1. Adjustments include integrated air nozzles for convective cooling of the quartz window, an optimized design of the reactor front and a radiation shield for enhanced cooling, and an optimized design of the ceria RPC cavity.

![Figure 4.1](image)

**Figure 4.1.** Schematic of the solar reactor installed in the solar tower in Spain. It is a directly irradiated cavity receiver-reactor containing a ceria RPC structure with dual-scale porosity. The detachable insulating jacket covering the outside of the steel shell is not shown here.

The four nozzles that guide compressed air onto the outer surface of the quartz window had to be integrated into the radiation shield of the solar reactor due to the limited space available in the solar tower, especially because of the movable flux measurement target that can be positioned directly in front of the reactor as described in section 4.1.3. A mounting structure for the quartz window with enhanced water cooling and an additional water-cooled radiation shield had to
be installed because the amount of spilled radiation that hits the reactor front but does not enter through the reactor’s aperture is much higher in the solar tower compared to the solar simulator.

*Ceria RPC cavity* – Two main conclusions about the design of a ceria RPC cavity were drawn from the experimental testing of the solar reactor in the high-flux solar simulator (chapter 2) and the numerical heat transfer model of the reactor (chapter 3):

- Increasing the mass loading of ceria in the reactor by means of increasing thickness or decreasing porosity of the RPC, both increasing its optical thickness, generally increases the mechanical strength and durability of the RPC, but does not result in increased reactor performance without effective volumetric absorption of the solar radiation and uniform heating of the ceria.
- More volumetric absorption of solar radiation can be accomplished by increasing the size of the millimeter-scale pores of the RPC. If at the same time the thickness of the struts of the RPC is increased to keep the porosity constant, the same mass of ceria can be heated more uniformly, resulting in a performance increase.

Based on these findings, a new RPC cavity was designed with larger millimeter-scale pores ($n_{\text{ppi}} = 7$ compared to the previously used $n_{\text{ppi}} = 10$) and a thickness $t_{\text{RPC}} = 35$ mm. Even larger pores are supposed to be beneficial, but cannot be fabricated with the current manufacturing method because this is the limit of porosity of the polyurethane foams used in the manufacturing process. A thickness of 35 mm was chosen as a tradeoff between cycling performance and mechanical stability. The manufacturing process for the RPCs was described in detail in section 2.1.2. It was slightly adapted by increasing the sintering duration and temperature to eight hours at 1700 °C (from one hour at 1600 °C), which was shown to increase the mechanical strength of the RPCs significantly [132].

Compared to the operation with the high-flux solar simulator where the solar reactor was horizontally facing the radiation source, in the solar tower the reactor is tilted downwards to the heliostat field with an inclination angle of around
40 degrees. To prevent structural failure in this orientation, a new design for the back of the ceria RPC cavity was developed. The dome-shaped back design, shown in Figure 4.2 (a), consists of eight wedge-shaped pieces that are inclined by 30 degrees compared to a flat back plane, and one central octagonal piece with chamfered edges. At the down-facing operating angle, this design keeps all the back pieces in compression against each other, just as the interlocking rings of side bricks hold each other in compression. The side of the RPC cavity consists of two rings of 16 RPC bricks each. Figure 4.2 (b) is a photograph of the back RPC pieces during installation when the reactor was positioned upright, showing the inclination of the wedge-shaped back pieces and the contact angle between a wedge-shaped piece and the central back piece. The channels cut into the back $\text{Al}_2\text{O}_3-\text{SiO}_2$ insulation to minimize contact between RPC and insulation and to facilitate gas flow exiting the reactor are also visible. The total ceria mass of all RPC bricks forming the cavity varied between 17.8 and 21.3 kg because RPCs were replaced during the course of experiments.

Figure 4.2. Detail view of the ceria RPC cavity with the dome-shaped back designed to prevent structural failure when the reactor is in operation in the solar tower, tilted by 40 degrees towards the heliostat field. (a) is a section view of the RPC cavity in its operational position as designed with CAD, while (b) is a photograph showing two wedge-shaped back pieces and the central octagonal back piece during installation in upright position.
4.1.2 Solar concentrating facility

An overview of the entire experimental facility located in Móstoles, Spain, is shown in Figure 4.3 [133]. The heliostat field was designed by IMDEA Energy Institute [134]. It consists of 169 heliostats with an area of 3 m² each, resulting in around 500 m² of total reflective area. All heliostats are curved with a focal length of 25 m for the first eight rows of heliostats closest to the solar tower and 30 m for the remaining six rows of heliostats. While conventional heliostats for electricity generation via concentrated solar power (CSP) usually are flat, curved heliostats are necessary to reach the higher concentration ratio needed to efficiently drive the solar thermochemical ceria cycle. This modular, high-flux heliostat field is able to meet the nominal operating condition of the solar reactor of 50 kW delivered into the 16 cm diameter reactor aperture, corresponding to a concentration of around 2500 kW m⁻².

![Figure 4.3](image)

**Figure 4.3.** Schematic of the experimental facility installed in Móstoles, Spain. Up to 169 heliostats with an area of 3 m² each concentrate sunlight onto a solar tower with an optical height of 15 m. Installed in the experimental level of the tower are the solar reactor and the power measurement system. The syngas produced in the solar reactor can be stored and processed to liquid hydrocarbon fuels on-site using the Fischer-Tropsch unit. All systems are centrally operated from the control room.
The solar reactor is placed on top of the solar tower with an optical height of 15 m, together with a power measurement system and peripheral components, described in detail in the following sections 4.1.3 and 4.1.4, respectively. The solar reactor is facing north and is tilted downwards by around 40 degrees in the direction of the heliostat field’s optical axis. On the ground next to the solar tower sits the Fischer-Tropsch unit, developed by HyGear in the Netherlands. It includes a buffer tank to store the syngas produced in the solar reactor, and can be used to produce liquid hydrocarbon fuels on-site. The experimental components, including the heliostat field, the solar reactor and the power measurement setup, are centrally operated from the control room located behind the heliostat field.

4.1.3 Power measurement system and methodology

In contrast to a solar simulator, the power delivered by the heliostat field cannot be held perfectly constant and varies in connection with many factors such as the direct normal irradiance (DNI) of the sun, the time of the year and the time of the day. Therefore, a more sophisticated power measurement system is necessary to estimate the power entering the solar reactor during the course of an experiment. Figure 4.4 (a) shows the arrangement of the solar reactor and the power measurement system in the solar tower [133]. Two different devices to measure power were installed: a water calorimeter and an optical flux measurement acquisition system (FMAS). The water calorimeter, developed by ETH Zurich, is mounted inside the same type of steel vessel as the solar reactor. The two vessels are placed 1.6 m apart, with the solar reactor installed west of the water calorimeter. Outside the circular, water-cooled fronts of reactor and calorimeter, porous Al$_2$O$_3$ insulation material is installed as a passive thermal shield to block radiation from entering into the experimental level of the solar tower during operation. The FMAS was developed by DLR in Germany [135]. It consists of a water-cooled, Al$_2$O$_3$ plasma-coated Lambertian target mounted on a linear belt which allows alignment with either receiver vessel for measurement, and a CCD camera with a telephoto lens mounted in the control room. In either of the two measurement positions, the center of the FMAS target is aligned with the optical axis of the heliostat field and the center of the respective receiver aperture, at a
distance of approximately 20 cm from the aperture plane. Before taking a measurement with the FMAS, it is automatically calibrated with a Gardon-type flux gauge embedded in the center left edge of the target. The power is calculated by integrating the compiled flux map over a circular area with a diameter of 16 cm, corresponding to the area of the apertures. If not in use for a measurement, the target is in standby position between the two receivers.

The details of the water calorimeter are shown in Figure 4.4 (b). It is designed to closely approximate the specifications of the solar reactor. The outer shell and the front section, including the cooling shield and the cavity aperture, are identical to the ones used for the solar reactor. The cavity of the calorimeter consists of aluminum front and back plates, and approximately 20 meters of coiled copper tubing, all coated with a black high-emissivity enamel. The cavity is thermally separated from the front, and the volume between the inner cavity and the outer shell is filled with rock wool insulation to minimize heat losses. Cold water enters to the hollow front plate and flows through the cooper tubing and internal channeling of the back plate, where it exits the calorimeter. The water flow rate is measured with a highly accurate electromagnetic flow meter (Endress+Hauser, Promag 33), and inlet and outlet temperatures of the water are recorded with four-wire Pt100 resistance thermometers. Using the measured temperature difference between inlet and outlet and the flow rate of water, the solar power entering the aperture can be calculated directly. Losses by reflection, emission, conduction and convection together were estimated to account for less than 1% of the incoming solar radiation at a power input of 50 kW, and the accuracy of a calorimeter measurement was specified as ±2%. Due to the calorimeter’s high accuracy and the additional error of an FMAS measurement imposed by the location of the Lambertian target slightly off the aperture plane, calorimeter measurements were directly used to assess the power entering the solar reactor. However, FMAS measurements were used to estimate the additional error introduced by the different locations of the calorimeter and the solar reactor.
Figure 4.4. (a) Detail view of the solar reactor and power measurement installation in the solar tower. The Lambertian target of the flux measurement acquisition system (FMAS) moves on a linear system, which allows alignment with either receiver vessel for measurement. The vessel at the east position contains a water calorimeter, and the west position receiver contains the solar reactor. (b) Cross section of the water calorimeter installed in the east receiver vessel, with indication of its main components.
The procedure to calculate the solar radiative power entering the reactor, $P_{\text{solar}}$, during a typical reduction cycle is shown in Figure 4.5. It shows the nominal RPC temperature in the solar reactor in red and the power measurements in black for both the water calorimeter and the FMAS positioned in front of the calorimeter and the reactor. Before a reduction step starts, the heliostats track from a nearby standby position to the calorimeter aperture position with the FMAS target positioned in front. Within less than 30 s, all heliostats move to the new aim position, and a first FMAS measurement is taken. The FMAS target then moves to its standby position, and the solar radiation enters the calorimeter. The calorimeter takes less than 180 s to approach a thermal steady state due to its low thermal mass, high thermal conductivity, and thin metallic walls between the cavity surface and the water channels. Once a steady measurement reading is recorded, the FMAS target is positioned in front of the solar reactor and the heliostat’s aim point is changed to the reactor aperture. Another FMAS measurement is taken, and when the target moves back to the standby position, full power enters the reactor’s aperture. When the reduction end temperature is reached, the measurement process is reversed. The FMAS target moves in front of the reactor, thereby interrupting power delivery to the solar reactor. An FMAS measurement is taken, followed by a calorimeter measurement and a second FMAS measurement at the calorimeter position. The steady calorimeter readings before and after the reduction step, 39.9 and 41.3 kW in the present case, are assumed to be equal to $P_{\text{solar}}$ at the beginning and the end of the reduction. The variation of delivered power mainly originates from tracking errors changing with time, and the DNI is assumed constant during the short reduction period of typically less than 15 min. This is justified because experiments were usually stopped when clouds appeared. Therefore, a linear change of $P_{\text{solar}}$ was assumed during reduction, and the grey area in Figure 4.5 corresponds to the total solar energy input to the reactor integrated over the reduction step, $Q_{\text{solar}}$. The difference between calorimeter and FMAS readings has two main reasons. First, the measurement plane of the FMAS is approximately 20 cm in front of the aperture plane, and second, additional power enters the reactor and the calorimeter by means of rays reflected on the conical aperture surface. However, because only the relative difference between FMAS measurements at the reactor
and the calorimeter positions are used to evaluate the inaccuracy imposed by measuring the power entering the reactor at the position of the calorimeter, these errors cancel out.

![Figure 4.5](image)

**Figure 4.5.** Representative measurement cycle to deduce the solar radiative power at the aperture of the solar reactor, $P_{\text{solar}}$. The nominal RPC temperature in the solar reactor is shown in red, along with power measurements with the water calorimeter and the FMAS in front of the calorimeter and the solar reactor in black. $P_{\text{solar}}$ is assumed to change linearly between steady calorimeter readings recorded before and after reduction, while the relative difference between FMAS measurements at the two positions is used to assess the inaccuracy imposed by measuring the power entering the reactor at the position of the calorimeter.

4.1.4 Reactor periphery and experimental procedure

The experimental setup installed in the solar tower is similar to the setup described in chapter 2.1.3 for experiments with the high-flux solar simulator. However, some adjustments were necessary, especially for the handling of water. The setup installed in the tower is schematically illustrated in **Figure 4.6** and shown in **Figure 4.7**, which is a photograph of the experimental level of the tower with indication of the major subsystems. Gas flow rates of Ar and $\text{CO}_2$ were
regulated using electronic mass flow controllers (Bronkhorst, EL-FLOW Select) and entered the reactor through tangential inlet ports behind the quartz window to form a vortex flow that protects the window from the deposition of particles. Liquid water was fed with a stepper motor driven positive displacement pump into an electrically heated steam generator (Adrop Feuchtemesstechnik GmbH, aTHMOS-RS-4). The steam was superheated to around 260 °C and fed through a separate port into the reactor cavity via an electrically heated, insulated Teflon pipe at 180 °C, therefore entering the solar reactor at roughly 200 °C. The temperature of the reacting ceria was monitored at four positions distributed over the back surface of the RPC using B-type thermocouples. The average of these temperature measurements was defined as the nominal RPC temperature \( T_{\text{RPC,nom}} \). The pressure inside the reactor was measured at the gas outlet and through a lateral port using Pirani gauge sensors combined with a capacitance diaphragm vacuum gauge (Leybold, THERMOVAC TTR 101 N). Up to four dry, multi-stage roots vacuum pumps (Pfeiffer Vacuum, ACP 40) were attached in parallel to the outlet port of the solar reactor via two parallel valves. A solenoid control valve (Bürkert Schweiz AG, valve type 2875, controller type 8605) was used to slowly evacuate the reactor at the beginning of the reduction step (path shown by the red arrows in Figure 4.6), and an electro-pneumatic valve with bigger nominal diameter (SMC Corporation, XLAV-50) was opened once the pressure was sufficiently low (< 200 mbar). During the oxidation step (path shown by the blue arrows in Figure 4.6), the vacuum pumps were bypassed by use of a smaller diameter electro-pneumatic valve (SMC Corporation, EVNB211B). Residual water was removed with a water-cooled glass condenser. Product gas composition was continuously (frequency 1 Hz) analyzed downstream using an electrochemical sensor for \( \text{O}_2 \) (Siemens, Ultramat 23), IR detectors for \( \text{CO} \) and \( \text{CO}_2 \) (Siemens, Ultramat 23), and a thermal conductivity based detector for \( \text{H}_2 \) (Siemens, Calomat 6). The gas composition was verified by gas chromatography (Agilent, 490 Micro GC). The produced syngas was either vented or collected and compressed in a 50 L gas cylinder to further process it with the on-site Fischer-Tropsch unit.
Figure 4.6. Simplified schematic of the experimental setup in the solar tower. During the endothermic reduction step, Ar flow is used to protect the quartz window and is pumped out together with the released O₂, while the reactor is under vacuum and irradiated with concentrated solar radiation. During the exothermic oxidation step, the ceria is re-oxidized with CO₂ and/or H₂O, therefore producing CO and/or H₂.
The operation procedure for the solar reactor during a representative experiment is shown in Figure 4.8. The reactor was first slowly preheated with a radiative power input $P_{\text{solar}}$ ramping up to around 10 kW for up to one hour, followed by a pre-cycle. During a pre-cycle, the reactor was heated with $P_{\text{solar}}$ approaching full power when the nominal reduction end temperature was reached. Reduction was terminated by placing the FMAS target in front of the reactor (thereby effecting $P_{\text{solar}} = 0$ kW) and a series of power measurements as described in section 4.1.3, simultaneously letting the reactor cool down to the nominal oxidation start temperature. The ceria was re-oxidized using $\text{CO}_2$ and/or $\text{H}_2\text{O}$. The primary cycle was initiated by evacuating the reactor using the vacuum pumps and focusing a defined number of heliostats onto the reactor’s aperture. The number of heliostats in operation was not changed during a single reduction step. To protect the quartz window from deposition of sublimated ceria and to govern the fluid flow when operating under vacuum conditions, an argon flow rate of 5 L min$^{-1}$ was introduced to the reactor directly behind the window. When the variable reduction end temperature was reached, re-oxidation was initiated by removing input power and repressurizing the reactor with $\text{CO}_2$ and/or $\text{H}_2\text{O}$. After the nominal RPC temperature decreased to the defined oxidation start temperature
by natural cooling, CO\textsubscript{2} and/or H\textsubscript{2}O was flown through the reactor at constant rates but variable ratio and ranges, producing a mixed flow in the outlet comprised of H\textsubscript{2}, CO and unreacted CO\textsubscript{2}, after the removal of excess water. The ceria was either fully re-oxidized or oxidation was stopped when a predefined criteria was met. After the oxidation of the last cycle was terminated, the solar reactor naturally cooled down, typically approaching ambient temperature the next morning. Experiments were usually terminated if clouds appeared. Up to eight consecutive cycles were performed per day with an average cycle time of around 50 minutes. An interesting characteristic of the solar concentrating facility can be seen in Figure 4.8: because tracking and optical errors increase the further away from solar noon, \(P_{\text{Solar}}\) steadily increases during every cycle in the morning and decreases during cycles after solar noon, even though the number of focused heliostats was constant for single cycles. The experimental facility is shown in operation in Figure 4.9.

**Figure 4.8.** Operation strategy for the solar reactor during a representative experiment, including a pre-heating phase, a pre-cycle, consecutive cycling, and a natural cooling phase. Indicated are the solar radiative power input to the reactor, \(P_{\text{Solar}}\), in black and the nominal RPC temperature in red.
Figure 4.9. Photographs of the experimental facility in operation: (a) the field of heliostats heating up the solar reactor in the tower during the reduction step; (b) the irradiated front of the solar reactor photographed with a neutral-density filter, showing the dark color of the ceria RPC cavity in the partially reduced state, (c) the solar tower with the glowing ceria RPC cavity while cooling down shortly after the end of the reduction step.
4.2 Results and discussion

4.2.1 Cyclic performance

The thermochemical performance of the solar reactor is assessed with the solar-to-fuel energy conversion efficiency, which is defined as

$$\eta_{\text{solar-to-fuel}} = \frac{Q_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{pump}} + Q_{\text{inert}}}$$  \hspace{1cm} (4.1)

\(Q_{\text{fuel}}\) is calculated as the amount of produced fuel integrated over an entire cycle multiplied with the higher heating value of the fuel (\(\Delta H_{\text{CO}} = 283 \text{ kJ mol}^{-1}\) and \(\Delta H_{\text{H}_2} = 286 \text{ kJ mol}^{-1}\)). Assuming complete re-oxidation, the energy content of the fuel produced in a cycle can also be calculated as \(Q_{\text{fuel}} = \Delta H_{\text{fuel}} \cdot 2 \int r_{O_2} dt\), where \(r_{O_2}\) is the rate of released oxygen during the reduction step. \(Q_{\text{solar}}\) is the total solar energy input integrated over the reduction step. \(Q_{\text{pump}}\) and \(Q_{\text{inert}}\) are the energy penalties associated with vacuum pumping and the consumption of the inert gas Ar during the reduction step, respectively, and are calculated as described in section 2.1.4.

For the operation of the solar reactor, pure \(\text{CO}_2\) splitting offers some advantages compared to the co-splitting of \(\text{H}_2\text{O}\) and \(\text{CO}_2\) or the oxidation with pure \(\text{H}_2\text{O}\). The main technical challenge when utilizing \(\text{H}_2\text{O}\) as oxidant is to make sure that no water condenses inside the solar reactor. At the same time, any unreacted water needs to be condensed and removed from the product gas mixture exiting the reactor to avoid damaging any instruments or processes located downstream. Even though the co-production of \(\text{H}_2\) and \(\text{CO}\) (syngas) with the solar reactor offers economic advantages for the subsequent production of liquid hydrocarbon fuels, syngas could also be produced from pure \(\text{CO}\) by adding the water-gas shift reaction as an additional process step [98].

Figure 4.10 shows the nominal RPC temperature, the reactor pressure as well as the \(\text{O}_2\) and \(\text{CO}\) evolution rates for three consecutive \(\text{CO}_2\) splitting cycles. The solar radiative power input \(P_{\text{solar}}\), averaged over each reduction step, was increased from 45.7±6.7 kW in the first cycle to 55.8±8.2 kW in the third cycle. In this experiment, the reactor was heated with variable \(P_{\text{solar}}\) from \(T_{\text{red,start}} = 700 \degree\text{C}\) to \(T_{\text{red,end}} = 1500 \degree\text{C}\) while continuously pumping vacuum and flowing Ar
On-sun demonstration of CO$_2$ and H$_2$O splitting

at $\dot{V}_{\text{Ar}} = 5.0$ L min$^{-1}$. Afterwards, the reactor was filled with CO$_2$ to atmospheric pressure while cooling down at $P_{\text{solar}} = 0$ kW. Starting at $T_{\text{ox,start}} = 900$ °C, the ceria was fully re-oxidized with $\dot{V}_{\text{CO}_2} = 50$ L min$^{-1}$ until $T_{\text{ox,end}} = 700$ °C, corresponding to $T_{\text{red,start}}$ of the following cycle. The molar ratio of CO produced to O$_2$ released was in the range of 2.03–2.06±0.21 for the three cycles, implying that the oxygen nonstoichiometry was fully exploited for fuel production. Figure 4.10 (b) shows the effect of varying $P_{\text{solar}}$ on three selected performance indicators, namely the volume of produced O$_2$ and CO, the reduction time $t_{\text{red}}$ and the solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$. Note that the error margin of $P_{\text{solar}}$ is not shown for simplicity. The experimental conditions and measured results of the third cycle with highest power input and efficiency are also summarized in Table 4.1.

The reduction time significantly decreased from 6.7 min at $P_{\text{solar}} = 45.7\pm6.7$ kW to 5.8 min at $P_{\text{solar}} = 52.8\pm7.8$ kW. Interestingly, it slightly increased for a further power increase to $P_{\text{solar}} = 55.8\pm8.2$ kW. This is attributed to a slight increase in actual reduction end temperature, even though the nominal end temperature was hold constant at $T_{\text{red,end}} = 1500$ °C. The nominal RPC temperature is defined as the average of four measurement points distributed over the back, non-irradiated surface of the RPC, and it was observed that the RPC generally heats up more uniformly with increasing cycle number. Because of the slightly higher reduction time at maximum power input, the amounts of produced O$_2$ and CO also increased to 45.8±0.9 L and 92.9±7.4 L, respectively. These trends of reduction time and fuel amount lead to a general trend of increasing efficiency with increasing power input, reaching a maximum of $\eta_{\text{solar-to-fuel}} = 5.6\pm1.0\%$ at $P_{\text{solar}} = 55.8\pm8.2$ kW, while the average efficiency of the three consecutive cycles was $\eta_{\text{solar-to-fuel}} = 5.2\pm1.0\%$. This trend, in correspondence to the results of the heat transfer model presented in chapter 3, suggest that even higher efficiencies could be reached by further increasing $P_{\text{solar}}$. However, this would require a more precise and costly solar concentrating facility and might detrimentally affect the mechanical stability of the ceria RPCs over a large number of cycles.
Figure 4.10. (a) Nominal RPC temperature, reactor pressure and O$_2$ and CO evolution rates as a function of time for three consecutive CO$_2$ splitting cycles with increasing average solar radiative power input $P_{\text{solar}}$ during reduction. (b) Volume of produced O$_2$ and CO, reduction time $t_{\text{red}}$ and efficiency $\eta_{\text{solar-to-fuel}}$ of the same cycles as a function of $P_{\text{solar}}$. The error margin of $P_{\text{solar}}$ is not shown for simplicity. Experimental conditions during reduction: $T_{\text{red, start}} = 700$ °C, $T_{\text{red, end}} = 1500$ °C, $V_{\text{Ar}} = 5.0$ L min$^{-1}$ at $p_{\text{reactor}} \leq 15$ mbar. Experimental conditions during oxidation: $T_{\text{ox, start}} = 900$ °C, $T_{\text{ox, end}} = 700$ °C, $V_{\text{CO}_2} = 50$ L min$^{-1}$ at atmospheric pressure. Ceria RPC mass $m_{\text{RPC}} = 17.8$ kg.
Table 4.1. Experimental conditions and results of the CO$_2$ splitting cycle with the highest average solar radiative power input during reduction, $P_{\text{solar}}$, and resulting maximum solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria RPC mass</td>
<td>$m_{\text{RPC}}$</td>
<td>17.8</td>
<td>kg</td>
</tr>
<tr>
<td>Average solar power input during reduction</td>
<td>$P_{\text{solar}}$</td>
<td>55.8±8.2</td>
<td>kW</td>
</tr>
<tr>
<td>Reduction start temperature</td>
<td>$T_{\text{red, start}}$</td>
<td>700</td>
<td>°C</td>
</tr>
<tr>
<td>Reduction end temperature</td>
<td>$T_{\text{red, end}}$</td>
<td>1500</td>
<td>°C</td>
</tr>
<tr>
<td>Oxidation start temperature</td>
<td>$T_{\text{ox, start}}$</td>
<td>900</td>
<td>°C</td>
</tr>
<tr>
<td>Oxidation end temperature</td>
<td>$T_{\text{ox, end}}$</td>
<td>700</td>
<td>°C</td>
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<tr>
<td>Ar flow rate during reduction</td>
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<tr>
<td>CO$_2$ flow rate during oxidation</td>
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<td>Reduction duration</td>
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<td>Oxidation duration</td>
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<td>Peak O$_2$ evolution rate</td>
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<td>L min$^{-1}$</td>
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<td>Total amount of O$_2$ released</td>
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<td>45.8±0.9</td>
<td>L</td>
</tr>
<tr>
<td>Average nonstoichiometry of ceria</td>
<td>$\delta$</td>
<td>0.039±0.001</td>
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<tr>
<td>Peak CO evolution rate</td>
<td></td>
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<td>L min$^{-1}$</td>
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<tr>
<td>Total amount of CO produced</td>
<td></td>
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<td>L</td>
</tr>
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<td>Average conversion of CO$_2$ to CO</td>
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<td>%</td>
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<td>Molar ratio CO/O$_2$</td>
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<td>2.03±0.21</td>
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<td>Vacuum pumping energy</td>
<td>$Q_{\text{pump}}$</td>
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<td>kJ</td>
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<td>Inert gas Ar separation energy</td>
<td>$Q_{\text{inert}}$</td>
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<td>kJ</td>
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<tr>
<td>Solar-to-fuel energy conversion efficiency</td>
<td>$\eta_{\text{solar-to-fuel}}$</td>
<td>5.6±1.0</td>
<td>%</td>
</tr>
</tbody>
</table>
The effect of changing the reduction end temperature on the performance of the solar reactor can be assessed with the instantaneous solar-to-fuel energy conversion efficiency. Figure 4.11 shows the instantaneous $\eta_{\text{solar-to-fuel}}$ and the O$_2$ yield as a function of the nominal RPC temperature for the CO$_2$ splitting experiment summarized in Table 4.1. The corresponding reduction times are indicated on the upper horizontal axis. Note that for this calculation, the O$_2$ measured after the end of the reduction step is neglected, which is why the maximum instantaneous $\eta_{\text{solar-to-fuel}}$ is slightly lower than the efficiency reported in Table 4.1. The tail of measured O$_2$ once $P_{\text{solar}}$ is set to zero at the end of reduction has two causes: temperature equilibration within the ceria RPC and diffusion and flow mixing effects of the mixture of O$_2$ and Ar in the reactor and the piping between the reactor and the gas analysis.

**Figure 4.11.** Instantaneous solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$ and O$_2$ yield as a function of the nominal RPC temperature for the CO$_2$ splitting cycle summarized in Table 4.1. Also indicated on the upper horizontal axis are the corresponding reduction times.
The \( \text{O}_2 \) yield increases exponentially with increasing RPC temperature due to the exponential correlation between oxygen nonstoichiometry \( \delta \) and temperature for ceria [63]. The efficiency \( \eta_{\text{solar-to-fuel}} \) also increases with increasing RPC temperature, but the slope decreases with temperature due to increasing heat losses and the energy consumed by the endothermic reduction reaction. This trend indicates that even higher \( \eta_{\text{solar-to-fuel}} \) could be reached by increasing the reduction end temperature. However, care must be taken to avoid local sublimation of ceria on the directly irradiated RPC surface, and further increasing the reduction end temperature might also detrimentally affect the structural integrity of the ceria RPC cavity over a larger number of redox cycles.

Figure 4.12. Instantaneous solar-to-fuel energy conversion efficiency \( \eta_{\text{solar-to-fuel}} \), CO yield and nominal RPC temperature as a function of the oxidation time for the CO\(_2\) splitting cycle summarized in Table 4.1.

During oxidation, prolonging the oxidation time until the ceria is completely re-oxidized maximizes the fuel yield per cycle, but also increases the temperature swing between start and end of reduction because the reactor cools down during oxidation. Figure 4.12 shows the instantaneous \( \eta_{\text{solar-to-fuel}} \), the CO yield and the nominal RPC temperature versus the oxidation time for the same CO\(_2\) splitting
cycle (summarized in Table 4.1). To calculate the instantaneous $\eta_{\text{solar-to-fuel}}$, the energy savings due to two effects were approximated: higher reduction start temperatures and less energy consumed by the endothermic reduction reaction if the oxidation time is shortened and the ceria is not fully re-oxidized. The efficiency peaks at $\eta_{\text{solar-to-fuel}} = 6.1\%$ after 8.0 min of oxidation and a fuel yield of 90.0 L of CO, which is 97% of the fuel produced at the end of the oxidation step. Therefore, $\eta_{\text{solar-to-fuel}}$ could be slightly increased by stopping the oxidation step before the ceria is fully re-oxidized. Furthermore, the share of unreacted CO$_2$ in the product gas increases with increasing oxidation time, which can have a detrimental effect on the efficiency of the downstream syngas processing. This is discussed in more detail in section 4.2.3.

4.2.2 Comparison to heat transfer model and energy balance

To get a further insight into the thermal performance of the solar reactor at its nominal operating condition, the heat transfer model of the solar reactor, described in detail in chapter 3, was used to simulate the CO$_2$ splitting cycle with maximum efficiency, summarized in Table 4.1. The geometry of the porous RPC domain was adapted to the design described in section 4.1.1 that is optimized for the operation in the solar tower. The solar concentrating facility was modelled as a set of rays uniformly distributed over the aperture area with a directional distribution that is also uniformly distributed and confined with a rim angle of 40 degrees, which closely approximates the specifications of the heliostat field.

In Figure 4.13, the nominal RPC temperature and the O$_2$ release rate are shown for the experiment (solid lines) and the simulation (dashed lines). The RPC temperature is slightly overestimated in the simulation, reaching 1557 °C at the end of the reduction step compared to 1500 °C for the experiment. When considering the uncertainty in the measurement of $P_{\text{solar}}$, the experimentally measured temperature profile lies well within the set of possible simulation results. The red shaded area indicates the possible nominal RPC temperatures when accounting for the uncertainty of $P_{\text{solar}}$ in the simulation, calculated by running the simulation with both the minimum and the maximum values for $P_{\text{solar}}$. The same trend can be seen for the rate of O$_2$ released. The experimentally
measured rates are smaller than the numerically calculated rates for $P_{\text{solar}} = 55.8$ kW at all times during the reduction step, due to the overestimation of the RPC temperature in the simulation. When accounting for the uncertainty of $P_{\text{solar}}$ though (grey shaded area in Figure 4.13), the experimental curve lies within the set of possible simulation results. The only significant difference between experiment and simulation occurs at the end of the reduction step. While the $O_2$ release stops within 30 seconds according to the simulation when the radiative power input is turned off at the end of the reduction, the experimentally measured $O_2$ rate decreases more slowly. The slower decrease is attributed to diffusion and flow mixing effects of the mixture of $O_2$ and Ar in the reactor and the piping between the reactor and the gas analysis.

Figure 4.13. Experimentally measured (solid lines) and numerically calculated (dashed lines) nominal RPC temperature as well as $O_2$ evolution as a function of time, during the reduction step and the subsequent natural cooling phase. While the dashed lines correspond to the simulation result with $P_{\text{solar}}$ set to the experimentally determined value of 55.8 kW, the shaded regions indicate the set of results when accounting for the measurement uncertainty of $P_{\text{solar}}$ in the simulation.
For $P_{\text{sol}} = 55.8 \text{ kW}$, the heat transfer model predicts an average temperature difference between the directly irradiated front and the back of the RPC of 229 °C at the end of the reduction step, and a maximum temperature within the entire RPC domain of $T_{\text{RPC,max}} = 1850 \degree \text{C}$, locally occurring at the directly irradiated inner RPC surface. This means that towards the back RPC surface, lots of energy is needed to heat the RPC, but the ceria does not contribute that much to the reaction due to the exponential decrease of reduction extent with decreasing temperature. Correspondingly, the ratio between the actually released $O_2$ and the amount of $O_2$ that could theoretically be released if all ceria mass would reach the maximum temperature within the RPC domain at the end of the reduction step is estimated to be 36%. The actually released amount of $O_2$ was measured during the corresponding experiment and is 45.8 L (see Table 4.1). The theoretical $O_2$ release at a uniform RPC temperature of $T_{\text{RPC,max}} = 1850 \degree \text{C}$, as predicted by the model, was calculated using the correlation for the oxygen nonstoichiometry $\delta$ that was also implemented in the model (see Table 3.1). An oxygen partial pressure of $p_{O_2} = 12 \text{ mbar}$ was assumed, which corresponds to the measured partial pressure at the end of the reduction step of the respective experiment. The correlation for $\delta$, developed by Ackermann [136], is based on an oxygen defect model that was fitted to experimental data available for temperatures up to $1500 \degree \text{C}$ and extrapolated to higher temperatures. It predicts a reduction extent of $\delta(T = 1850 \degree \text{C}, p_{O_2} = 12 \text{ mbar}) = 0.109$, which corresponds to an oxygen volume of 127 L for the experimental ceria mass loading of $m_{\text{RPC}} = 17.8 \text{ kg}$. The calculated ratio of 36% highlights that the performance of the solar reactor could be further increased if the ceria RPC could be heated more uniformly. As shown in the previous chapter 3, more volumetric absorption of the incoming solar radiation is needed for more uniform heating of the ceria structure, which could be achieved for example by increasing the RPC macropore size or with advanced ceria structures that feature a gradient in porosity.

The energy balance according to the numerical heat transfer model is visualized in Figure 4.14 for the cycle at $P_{\text{sol}} = 55.8 \text{ kW}$. The entire pie corresponds to $Q_{\text{sol}}$, the solar radiative energy input integrated over the reduction step. Indicated are losses by reradiation from the hot cavity, the change in sensible
heat content of the RPC, the remaining reactor components (Al₂O₃–SiO₂ insulation, aluminum front, reactor shell and insulating jacket), the energy consumed by the endothermic reduction reaction, losses by reflection and absorption of solar radiation at the quartz window, the conductive heat loss to the water-cooled reactor front, and other heat losses, together with their shares in $Q_{\text{solar}}$. Other heat losses include convection and radiation at the outer reactor surfaces and reflection of incoming solar radiation inside the reactor cavity.

**Figure 4.14.** Energy balance of the CO₂ splitting cycle at a solar radiative power input of $P_{\text{solar}} = 55.8$ kW, which resulted in the highest demonstrated solar-to-fuel energy conversion efficiency (corresponding experimental values are summarized in Table 4.1). Other heat losses include convection and radiation at the outer reactor surfaces and reflection of incoming solar radiation inside the reactor cavity. The entire pie corresponds to $Q_{\text{solar}}$, the solar radiative energy input integrated over the reduction step.

Losses by reradiation from the hot cavity account for 21.0% of the energy input. By far the most significant share is the energy needed for sensible heating of the reactor components, which highlights again the importance of implementing heat recovery in order to further boost the efficiency of such reactor technology in the future. 43.3% of $Q_{\text{solar}}$ is used for sensible heating of the RPC and 15.1% for sensible heating of the remaining reactor components. The energy consumed by the endothermic reduction reaction of ceria accounts for 10.5% of the solar energy input, and 7.1% is lost by reflection and absorption at the quartz window.
2.1% of $Q_{\text{solar}}$ is lost by conduction to the water-cooled aluminum front, while the remaining heat losses by convection and radiation at the outer reactor surfaces and reflection of incoming solar radiation inside the reactor cavity account for 0.5% or less each.

Apart from the solar radiative energy entering the reactor through the aperture ($Q_{\text{solar}}$), for the operation of the solar reactor energy is also needed to drive the vacuum pumps ($Q_{\text{pump}}$) and to provide the inert gas Ar that is consumed during the reduction step ($Q_{\text{inert}}$), which is accounted for in the definition of the solar-to-fuel energy conversion efficiency (equation (4.1)). Compared to the solar radiative energy input, both energy penalties are relatively small, with $Q_{\text{pump}}$ and $Q_{\text{inert}}$ amounting to 2.6% and 0.5% of $Q_{\text{solar}}$, respectively.

### 4.2.3 Optimization of syngas composition

Different operational modes for the solar reactor are conceivable in order to produce syngas with a composition that is suitable for Fischer-Tropsch synthesis. H$_2$ and CO can either be produced separately with pure splitting of H$_2$O and CO$_2$ in different redox cycles or simultaneously by co-feeding H$_2$O and CO$_2$ during the oxidation step. Figure 4.15 summarizes an exemplary cycle for the simultaneous production of H$_2$ and CO. It shows the nominal RPC temperature, the reactor pressure and the flow rates of produced O$_2$, CO and H$_2$. The solar radiative power input $P_{\text{solar}}$, averaged over the reduction step, was 42.0±6.2 kW. In contrast to pure CO$_2$ splitting, where the reactor pressure increased with increasing amount of O$_2$ released during the reduction step, the reactor pressure slowly decreased from around 70 mbar to 25.2±3.8 mbar at the end of the reduction step. This is attributed to the removal of liquid water that accumulated inside the solar reactor during the previous oxidation step. Because the reactor front and the aperture are water-cooled, local spots of the solar reactor retain temperatures below the boiling point of water. Therefore, a small amount of the water that enters the reactor as steam during the oxidation step condenses and remains in the reactor until the next reduction step. When the reactor pressure is decreased at the beginning of the next cycle, the liquid water evaporates again because of the lower boiling temperature under vacuum, but the pressure only
slowly decreases until all residual water is removed from the solar reactor. The extent of water condensation during oxidation was decreased considerably by controlling the cooling water flow rate but could not be avoided completely. After the target reduction end temperature of 1500 °C was reached, the reactor was repressurized with a mixed flow of 0.033 mol s⁻¹ of H₂O and 10 L min⁻¹ of CO₂, corresponding to a molar feeding ratio of 4.5. Starting at a nominal RPC temperature of 900 °C, the same amount of steam and CO₂ was fed to the reactor to produce a mixed flow of H₂ and CO together with unreacted H₂O and CO₂.

Figure 4.15. Nominal RPC temperature, reactor pressure as well as O₂, CO and H₂ evolution rates of an exemplary cycle for the simultaneous splitting of CO₂ and H₂O. Experimental conditions during reduction: \( P_{\text{solar}} = 42.0 \pm 6.2 \text{ kW}, T_{\text{red,\ start}} = 632 \text{ °C}, T_{\text{red,\ end}} = 1502 \text{ °C}, \dot{V}_{\text{Ar}} = 5.0 \text{ L min}^{-1} \) at \( p_{\text{reactor}} \leq 70 \text{ mbar} \). Experimental conditions during oxidation: \( T_{\text{ox,\ start}} = 900 \text{ °C}, T_{\text{ox,\ end}} = 654 \text{ °C}, \dot{m}_{\text{H₂O}} = 0.033 \text{ mol s}^{-1}, \dot{V}_{\text{CO₂}} = 10 \text{ L min}^{-1} \) at atmospheric pressure. Ceria RPC mass \( m_{\text{RPC}} = 18.1 \text{ kg} \).

Both H₂ and CO production peaked shortly after oxidation started at rates of 9.4±0.8 L min⁻¹ for H₂ and 5.4±0.4 L min⁻¹ for CO and decreased slowly until the ceria was fully re-oxidized after 24.0 min of oxidation at a nominal RPC temperature of 654 °C. Integrated over the entire cycle, a total amount of 36.2±0.7 L O₂, 48.9±3.9 L H₂ and 24.4±2.0 L CO was produced. This
corresponds to a molar ratio of H$_2$ and CO to O$_2$ of 2.03±0.21, indicating that the oxygen nonstoichiometry was fully exploited for fuel production, and a ratio of H$_2$ to CO of 2.01±0.35. The corresponding solar-to-fuel energy conversion efficiency was 4.1±0.8%. Note that the operating conditions were not optimized for maximum efficiency. The efficiency could be further increased especially when operating at a higher solar radiative power input $P_{\text{solar}}$, as demonstrated in section 4.2.1 for pure CO$_2$ splitting.

By adjusting different operational parameters of the solar reactor, the composition of the produced syngas can be controlled. Figure 4.16 shows the ratio of H$_2$ and CO in the produced syngas as a function of the molar ratio between H$_2$O and CO$_2$ fed to the reactor during oxidation for different feeding ratios at oxidation start temperatures of $T_{\text{ox, start}} = 900$ °C and 800 °C. The remaining operating conditions of the solar reactor were kept as constant as possible: the solar radiative power input $P_{\text{solar}}$, averaged over the reduction step, was in the range of 36.0–42.0±6.2 kW while the reactor was under vacuum pressure of less than 80 mbar, the reduction end temperature was $T_{\text{red, end}} = 1500±2$ °C, and complete re-oxidation was performed with a total flow rate of $\dot{V}_{\text{H}_2\text{O}} + \dot{V}_{\text{CO}_2} = 70$ L min$^{-1}$ (volume flow rate calculated at 373.15 K and 101’325 Pa for H$_2$O and at 273.15 K and 101’325 Pa for CO$_2$) at atmospheric pressure.

The dashed line is a linear fit of the results with an oxidation start temperature of 900 °C, showing a clear trend of increasing ratio of H$_2$ to CO in the product gas with increasing molar feeding ratio of H$_2$O to CO$_2$. According to these results, if the oxidation start temperature is set to 900 °C, H$_2$O and CO$_2$ has to be fed to the reactor at a molar ratio between 4.43 and 5.25 in order to produce syngas with a ratio of H$_2$ to CO in the range of 2–2.5 that is suitable for Fischer-Tropsch synthesis. Alternatively, the syngas composition can also be modified by changing the oxidation start temperature. Decreasing the oxidation start temperature to 800 °C resulted in a ratio of H$_2$ to CO of 2.94±0.51 compared to 2.01±0.35 at $T_{\text{ox, start}} = 900$ °C with the same molar H$_2$O/CO$_2$ feeding ratio of 4.46±0.23. This effect can be explained at least in part because H$_2$O dissociation is thermodynamically favored at lower temperatures compared to the dissociation of CO$_2$ [87].
In section 4.2.1, the effect of stopping the oxidation step before the ceria is fully re-oxidized on the solar reactor efficiency was discussed. The extent of oxidation also has an effect on the composition of the produced syngas, and complete re-oxidation is only possible if the oxidant is provided in excess. Unreacted H$_2$O can easily be separated from the gas mixture exiting the solar reactor via condensation, but the removal of excess CO$_2$ is more complex. For the Fischer-Tropsch process, the removal of unreacted CO$_2$ from the syngas is not always necessary, but the efficiency of the process usually decreases with increasing CO$_2$ content [15].

Figure 4.17 shows the yield of H$_2$ and CO as well as the cumulative concentrations of H$_2$, CO and CO$_2$ in the accumulated syngas as a function of the oxidation time for the experiment that was presented in Figure 4.15. The cumulative concentration is defined as the concentration of the respective component in the gas that accumulated since the beginning of the oxidation step (oxidation time = 0 min), after the removal of excess water through condensation.
After 2.0 min of oxidation time, the cumulative concentration of fuel in the accumulated syngas reached a maximum with 46.0% H₂ and 25.2% CO, the remaining 28.8% being unreacted CO₂. However, only 16.1 L of H₂ and 8.9 L of CO is produced after 2.0 min of oxidation, corresponding to 34.1% of the total fuel yield for complete re-oxidation. If the oxidation is stopped after 7.0 min for example, already 86.0% of the potential fuel is produced (41.2 L H₂ and 21.8 L CO), and the cumulative concentrations of H₂ and CO in the syngas are still relatively high with 37.3% H₂ and 19.7% CO. If oxidation is further carried on, the additional amount of fuel that can be produced is relatively small, but the accumulated syngas is diluted with unreacted CO₂, which eventually reaches a cumulative concentration exceeding 70% for oxidation times of 20 min and more. The molar ratio between H₂ and CO in the produced syngas increased slightly from a minimum of 1.81 at an oxidation time of 1.2 min to a ratio of 2.0 at the end of oxidation.

![Figure 4.17](image_url)

*Figure 4.17.* Fuel yield of H₂ and CO and cumulative concentrations of H₂, CO and CO₂ in the accumulated syngas as a function of the oxidation time for the experiment presented in *Figure 4.15.*
4.2.4 Long-term operation

Stable performance of the solar reactor over a large number of redox cycles is essential for any potential commercial application. The morphological stability of the same type of RPCs with dual-scale porosity that is used here was previously demonstrated with 227 consecutive redox cycles in a 4 kW solar reactor [51] and with 500 consecutive cycles in an IR furnace [53]. For the solar reactor of this study, the structural integrity of the self-supporting ceria RPC structure is equally important. In order to assess the cycling stability of the ceria RPC cavity and to produce a significant amount of syngas that can be processed to liquid hydrocarbon fuels on-site using the Fischer-Tropsch unit, multiple consecutive cycles were performed with the solar reactor. Based on the findings from the previous section 4.2.3, appropriate operating conditions for the solar reactor were chosen to produce syngas with a composition that is suitable for Fischer-Tropsch processing. An ideal composition of the syngas for processing with the cobalt-based Fischer-Tropsch reactor is a molar ratio of H₂ to CO of around 2.15 [15]. In total, 62 consecutive cycles were performed using the same RPC cavity with a ceria mass loading of \( m_{\text{RPC}} = 21.3 \text{ kg} \).

*Figure 4.18* shows the nominal RPC temperature as well as the concentrations of O₂, H₂, CO and CO₂ measured in the product gas mixture leaving the solar reactor, after the removal of unreacted H₂O, for a representative cycle. For all cycles, the reactor was evacuated to vacuum pressures of less than 100 mbar before the solar power was applied to heat the ceria RPC to the target nominal temperature of 1450 °C. Shortly after the target temperature was reached, the reactor was slowly repressurized with a mixed flow of H₂O and CO₂ at a molar ratio of 5.2. Once the ceria RPC temperature naturally cooled down to the oxidation start temperature of 900 °C, a mixture of 0.039 mol s⁻¹ of H₂O and 10 L min⁻¹ of CO₂, corresponding to a molar feeding ratio of 5.2, was flown through the reactor. Oxidation was stopped when the measured CO₂ concentration approached 80% in order to limit the amount of residual CO₂ in the collected syngas. For the exemplary cycle shown in *Figure 4.18*, this corresponds to an oxidation time of 6.8 min during which a total amount of 29.5±2.4 L H₂ and 13.3±1.6 L CO was produced.
Figure 4.18. Nominal RPC temperature and concentrations of O₂, H₂, CO and CO₂ in the product gas leaving the solar reactor for a representative cycle during the long-term operation of the reactor. Experimental conditions during reduction: \( P_{\text{solar}} = 37.9 \pm 5.7 \) kW, \( T_{\text{red,start}} = 812 ^\circ \text{C}, T_{\text{red,end}} = 1447 ^\circ \text{C}, \dot{V}_{\text{Ar}} = 5.0 \text{ L min}^{-1} \) at \( p_{\text{reactor}} \leq 100 \text{ mbar} \). Experimental conditions during oxidation: \( T_{\text{ox,start}} = 900 ^\circ \text{C}, T_{\text{ox,end}} = 853 ^\circ \text{C}, \dot{n}_{\text{H₂O}} = 0.039 \text{ mol s}^{-1}, \dot{V}_{\text{CO₂}} = 10 \text{ L min}^{-1} \) at atmospheric pressure. Ceria RPC mass \( m_{\text{RPC}} = 21.3 \text{ kg} \).

The nominal RPC temperature at the end of the reduction step as well as the total volume of H₂ and CO produced per cycle is shown in Figure 4.19 for all 62 consecutive cycles. These cycles were conducted during nine experimental days between the 5th and the 29th of July 2019 with a total experimental time of more than 55 hours. Except for one day when the experiment was stopped early due to clouds, between six and eight cycles were conducted every day with an average cycle duration of 53.4 minutes. During the first 45 cycles (region I in Figure 4.19), the target reduction end temperature of 1450 °C was reached with a maximum deviation of 18 °C for all cycles except for the 24th cycle. During this cycle, the reduction step had to be interrupted at a nominal RPC temperature of 1393 °C because not enough power was available anymore to further heat the ceria RPC due to the late hour of operation. Also indicated are linear fits of the reduction end temperature and the total yield of H₂ and CO per cycle. As a result of the approximately constant operating conditions, the total fuel yield for both
Figure 4.19. Nominal ceria RPC temperature at the end of the reduction step and total volume of produced H$_2$ and CO per cycle as a function of the cycle number for 62 consecutive redox cycles performed with the same RPC cavity with a ceria mass loading of $m_{\text{RPC}} = 21.3$ kg. Also indicated are linear fits of these temperatures and fuel yields, separately for the first 45 cycles (region I) with relatively constant or slightly increasing trends and for the last 17 cycles (region II) with generally lower levels and decreasing trends for increasing cycle number.
H₂ and CO was relatively constant. There is no visible trend of decreasing fuel yield, and the volume of H₂ produced per cycle even slightly increased with increasing cycle number.

During the last 17 cycles (region II of Figure 4.19), the variation in the reduction end temperature was larger, with a general trend of lower temperatures compared to region I and decreasing temperatures with increasing cycle number. The reason why the temperature stayed below the target reduction end temperature of 1450 °C during several cycles is the way the solar reactor was controlled. For safety purposes and in order to avoid local structural damage to the RPC, the reduction step was aborted whenever one of the four thermocouples distributed over the back surface of the RPC measured a temperature of 1550 °C. Due to the distribution of the incoming solar radiation over the irradiated RPC surface that was not perfectly uniform, the back of the ceria RPC cavity usually heated faster than the sides, but the temperature deviation from the nominal RPC temperature, defined as the average of the four measurement points, normally stayed below 100 °C. However, during the last two days of operation, a maximum temperature of 1550 °C was measured several times due to local structural degradation of the RPC resulting in faster heating of the back of the ceria RPC cavity. A direct link between the total fuel yield per cycle and the reduction end temperature can be observed. Lower volumes of H₂ and CO were produced during cycles with lower reduction end temperatures and there is a trend of decreasing fuel volumes with increasing cycle number and generally lower fuel yields compared to region I, in accordance with the trend for the reduction end temperature of these cycles.

The solar-to-fuel energy conversion efficiency averaged over the 62 consecutive cycles was 1.7±0.4%. Note that the operating conditions during these cycles were not optimized for maximum efficiency (as described in section 4.2.1) but for syngas yield and composition, with the aim of producing a significant amount of syngas suitable for Fischer-Tropsch processing during minimum experimental time. Summed up over all 62 consecutive cycles, 5191±364 L of syngas were produced with a composition of 31.8±3.2% H₂, 15.2±2.4% CO and 53.0±3.6% CO₂. Unreacted H₂O was separated with a water-cooled glass condenser located behind the gas outlet of the solar reactor. The syngas composition corresponds
to a molar ratio between H₂ and CO of 2.1, which fits the targeted syngas quality for Fischer-Tropsch synthesis. Most of the produced syngas was collected and stored on-site in a pressurized gas cylinder to further process it to liquid hydrocarbon fuels. However, especially during the first two days of operation, some of the produced syngas had to be vented because of a malfunction of the gas compressor and technical difficulties with the interface between the solar reactor and the gas compression system. Overall, around 91% of the produced syngas was collected and stored and subsequently processed with the on-site Fischer-Tropsch reactor. The analysis of the quantity and the composition of the product mixture was ongoing by the time of completion of this thesis.

With this experimental campaign, the technical feasibility of solar thermochemical H₂O and CO₂ splitting via ceria redox cycling was demonstrated under real-world conditions and at a relevant scale. Despite considerable progress, the ceria RPC is still the most delicate component of the solar reactor. Stable reactor performance was shown over 45 consecutive redox cycles without any visible degradation, but for the remaining 17 cycles, the performance slightly decreased, presumably due to the deterioration of the ceria RPC caused by the formation of cracks. These cracks mainly result from stresses induced by thermal and chemical expansion of ceria during reduction [65]. For any commercial application, a ceria RPC would probably have to withstand thousands of cycles before it could be repaired or replaced. Therefore, further progress with the manufacturing of mechanically strong ceria structures is essential. Adaptions of the manufacturing process or changes of the design specifications could further increase the mechanical strength of the RPCs. With lower maximum temperatures or smaller heating rates and temperature gradients, the formation of cracks could be alleviated but at the expense of lower reactor performance in terms of energy conversion efficiency. Even if the formation of cracks cannot be avoided, adjustments of the design of the solar reactor could help to prevent structural failure of the ceria RPC cavity. For example, a self-supporting design hold in place by gravity could be implemented more easily if the solar reactor’s aperture is facing upwards when operated with a solar concentrating facility in beam-down operation.
4.3 Summary and conclusions

Solar thermochemical splitting of CO$_2$ and H$_2$O has been demonstrated with the 50 kW solar reactor using a solar concentrating facility located in Móstoles, Spain. The experimental facility consisted of three different subsystems: a high-flux solar concentrating heliostat field and tower, the solar reactor system including a dedicated power measurement setup, and a gas-to-liquid conversion plant to process the produced syngas to liquid hydrocarbon fuels on-site via Fischer-Tropsch synthesis. The solar reactor, installed on top of the solar tower, featured an adapted ceria RPC cavity for structural integrity in its operation position facing down onto the heliostat field and for maximum performance. For CO$_2$ splitting, a maximum solar-to-fuel energy conversion efficiency of 5.6±1.0% was experimentally demonstrated at a solar radiative power input of 55.8±8.2 kW. Simulating the same experiment with a transient heat transfer model revealed that 58.4% of the solar energy input was used for sensible heating of the ceria and the bulk reactor components, which highlights the need to implement solid heat recovery in order to further increase the efficiency of similar reactor technology in the future. For the co-splitting of H$_2$O and CO$_2$, different possibilities to control the composition of the produced syngas were demonstrated. At optimal operating conditions, 62 consecutive redox cycles were performed with the same ceria RPC cavity. Constant fuel yields were observed for the first 45 cycles, but for the remaining 17 cycles, the reduction end temperature had to be slightly decreased due to local structural degradation of the RPC, resulting in lower fuel yields per cycle. The syngas produced during these 62 cycles was collected and stored to further process it to liquid hydrocarbon fuels on-site via Fischer-Tropsch synthesis. These results demonstrate the feasibility of solar thermochemical H$_2$O and CO$_2$ splitting via ceria redox cycling at a relevant scale for an industrial application and at realistic operating conditions. Critical issues that remain are the structural integrity of the ceria RPC cavity over a large number of consecutive redox cycles and the technically challenging implementation of solid heat recovery to further increase the solar reactor efficiency.
5 Outlook and research recommendations

The ultimate goal of research on solar thermochemical splitting of H\textsubscript{2}O and CO\textsubscript{2} is to find a way to produce transportation fuels that can replace currently used fossil fuels in an economical manner. Although there has been substantial progress over the last decades, major improvements are still necessary in order to achieve this goal. For a future solar fuels production plant, the solar reactor technology is the least developed process step. Other necessary steps, such as capturing CO\textsubscript{2}, concentration of sunlight and liquid fuel production via Fischer-Tropsch synthesis, are further developed and commercial solutions are already available. Therefore, in order to decrease cost, most of the future research needs to focus on making the process step of splitting H\textsubscript{2}O and CO\textsubscript{2} into syngas more efficient.

In order to increase the performance of a solar thermochemical reactor for H\textsubscript{2}O and CO\textsubscript{2} splitting, research should continue on all scales, starting from fundamental research on materials to system analyses and optimization for the optimal integration of a solar reactor technology into a fuel production plant. Material research should continue on screening and testing of potential candidates for redox cycling, such as doped ceria or perovskites. Finding a material that reaches higher reduction extents or has lower reduction temperatures compared to ceria but similar oxidation characteristics could be beneficial not only for the efficiency of the solar reactor but also for the long-term stability of the active material structure.

On the scale of redox material structures, finding a way to manufacture ceria structures with larger pores or a gradient in porosity for better volumetric absorption of radiation and more uniform heating could further increase the reactor efficiency while decreasing the mechanical load on the material caused by high maximum temperatures. While there is a limit on pore size for RPCs,
novel manufacturing techniques such as additive manufacturing even offer the possibility to fabricate ordered porous structures with a tailored porosity gradient [95]. However, especially for complicated structures with ordered porosity, the geometry needs to be carefully optimized in order to outperform currently used RPC structures, for example with the use of suitable numerical models. Furthermore, verification of the long-term stability of RPC structures should be extended to more cycles. While relatively stable fuel production rates were shown over a few dozen cycles in the present work and a few hundred cycles with different reactors [51, 53], a structure would presumably have to withstand several thousands of cycles before it could be repaired or exchanged in a competitive industrial application. The possibility to repair broken ceria structures, to recycle the ceria of used structures for the fabrication of new ones as well as the automation of the fabrication process of ceria structures should also be investigated.

Apart from adapting the ceria structures, there are several other ways to improve the presented cavity receiver-reactor. The potential of actively cooling the ceria RPC structure between reduction and oxidation should be investigated. Active cooling could be realized for example by flowing a large amount of an inert gas such as nitrogen or argon through the structure after the end of the reduction step. The extracted heat could be stored in a separate thermal storage unit or used directly to preheat a second solar reactor if multiple reactors are operated simultaneously with a time shift between the cycles of different reactors. Alternatively, the extracted heat could be used to drive other processes needed for the operation of the solar reactor, such as evaporating water, preheating steam and CO₂, or driving the vacuum pumps, provided the heat can be converted to electricity first. Extracted heat could also be used to drive other process steps in a fuel production plant, either directly or via conversion to electricity, such as capturing CO₂ from ambient air or compressing produced syngas. Actively cooling the solar reactor between reduction and oxidation would also decrease the cycle time, therefore increasing the amount of fuel produced per time unit. However, the influence of rapid active cooling of ceria RPCs on their long-term mechanical stability is unknown and should be assessed.
Possibilities to decrease the content of unreacted CO\textsubscript{2} in the product gas mixture should be investigated. Besides changing operational parameters of the solar reactor to increase the conversion of reactant gases, this could be achieved for example by refeeding the product gas mixture, which is composed of CO\textsubscript{2}, CO and H\textsubscript{2} after removal of excess water, into the reactor during oxidation. A high CO\textsubscript{2} utilization is not only important because CO\textsubscript{2} is a valuable feedstock, but also because a large amount of unreacted CO\textsubscript{2} in the accumulated product gas mixture could increase the necessary pumping and compression work or degrade the efficiency of the subsequent liquid fuels production process. The conversion of H\textsubscript{2}O to H\textsubscript{2} should also be analyzed in more detail because of the significant amount of energy needed to evaporate the water. In addition, future solar reactors should be designed such that steam condensation is completely avoided inside the reactor, for example with better thermal separation of water-cooled parts or using a different cooling liquid at higher temperatures. Steam condensation limits the performance of the solar reactor because condensed water does not directly transform to H\textsubscript{2} and needs to be pumped out of the reactor in the subsequent reduction step, thereby limiting the minimum achievable pressure during reduction.

Possible ways to further increase the reactor efficiency also include operating at lower pressures during the reduction step or heating the solar reactor at atmospheric pressure and only applying vacuum at the end of the reduction step. By decreasing the pressure, more oxygen could be released and consequently more fuel could be produced per cycle. However, the energy needed to reach such low pressures should be assessed carefully to ensure that it remains at a reasonable proportion to the energy content of the produced fuel. By adapting the operating mode and applying vacuum towards the end of the reduction step while the ceria is heated at atmospheric pressure, the theoretical pumping work could be decreased because the released O\textsubscript{2} would be pumped at the highest possible pressure. Such an operating mode was proposed for example for a particle based reactor concept with multiple reduction chambers, and is expected to significantly decrease the required pumping work [137].
For the experiments presented in this work, the oxygen released by the ceria during the reduction step was vented together with argon that was used to protect the quartz window from the deposition of particles. In a future, commercial fuel production plant, the economic value of the technology could be increased by collecting the oxygen and selling it as a valuable feedstock for other processes. However, the separation of the mixture of oxygen and argon is costly and requires additional energy. Therefore, adaptations to the solar reactor design and operation should be assessed such that the reduction step can take place without the use of an inert gas. This could include a detailed computational assessment of the flow field inside the reactor and design changes to prevent any backflow from the main cavity of the reactor to the section of the window, or switching to $\text{O}_2$ as protective gas. With the latter approach, the fuel production capacity per cycle would decrease slightly because of the increased oxygen partial pressure during reduction, but the oxygen leaving the reactor could be used directly without the need for purification.

Apart from the solar reactor, the remaining subsystems of the solar fuels pilot plant presented in chapter 4 could also be improved. The inaccuracy of the power assessment technique could be decreased by correcting for the error introduced when measuring the power with the water calorimeter, which is located at a different position than the solar reactor. However, in order to do so, the systematic error would need to be assessed in detail, for example by means of an accurate ray tracing model of the heliostat field that also includes the water calorimeter, the solar reactor and the FMAS. By improving the aiming and tracking algorithm of the heliostats, the optical efficiency and maximum deliverable power of the heliostat field could be increased, while decreasing the thermal load on the solar reactor system by spilled radiation and increasing the available experimental time per day.

On the scale of complete fuel production plants, system-scale modelling should be applied to optimally integrate and couple the individual technologies, such as the concentrating facility, the solar thermochemical reactor and the liquid fuels synthesis unit. While some designs might be beneficial for the efficiency of individual subsystems, they do not necessarily maximize the performance of the
overall system. An example is a beam-down orientation solar concentrating field design where the concentrated sunlight is redirected with a secondary mirror on top of the tower to the solar reactor sitting on the ground. Such a design would decrease the optical efficiency of the concentrating facility, but might be beneficial for the long-term stability of the ceria structures because a self-supporting design hold in place by gravity could be implemented more easily when the solar reactor is facing upwards. Other trade-offs include the aperture size of the solar reactor and the conversion of H₂O and CO₂. A small reactor aperture increases the reactor’s efficiency, but at the same time increases the complexity and cost of the solar concentrating facility and decreases its optical efficiency because of the need for higher concentration ratios. A future commercial solar fuels production plant is typically envisioned to consist of an array of solar reactors placed next to each other on the top of a solar tower. With such a configuration and the incorporation of compound parabolic concentrators (CPC) in front of the reactor’s apertures, the optical losses of the solar concentrating facility could be lowered. The exact design, orientation, and the size of the individual solar reactors could be determined with a holistic model, keeping in mind the size limitation of the solar reactor due to manufacturing and stability limitations of the currently used ceria structures. The energy efficiency of the solar reactor is generally higher at lower conversions of H₂O and CO₂, but there is an energy penalty for heating and evaporating (in the case of H₂O) excess reactant gas as well as for CO₂ removal from the product gas mixture or to compress the unreacted CO₂ together with the syngas if it is not removed. A large amount of unreacted CO₂ in the produced syngas also decreases the efficiency of the downstream Fischer-Tropsch synthesis. Furthermore, it could be beneficial for the efficiency of the entire system to separately produce H₂ and CO in different cycles, or to dedicate some solar reactors to H₂ production only while others are dedicated to CO production. To answer such questions and to generally optimize the operation of the solar reactor for an ideal integration with other subsystems, the numerical model presented in chapter 3 could be extended to also include the oxidation step. However, a more simplified reactor model, for example a transient, one-dimensional model with the Rosseland diffusion approximation for radiation modelling, would be better suited to quickly assess
a large number of different parameters because of the drastically lower computational complexity.\textsuperscript{1}

An in-depth techno-economic evaluation of the entire process chain from ambient air and water to liquid hydrocarbon fuels could also serve to assess in detail the expected production cost and to further evaluate the potential of the technology to eventually become economically competitive.

\footnote{A suitable model was developed within the framework of C. Larrea, “Assessment of a 50 kW solar reactor for thermochemical splitting of CO\textsubscript{2},” Master Thesis, ETH Zurich, 2018, supervised by S. Zoller.}
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