4 kW solar reactor technology for splitting of H₂O and CO₂ with a temperature – pressure swing redox cycle

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4 kW solar reactor technology for splitting of H₂O and CO₂ with a temperature – pressure swing redox cycle

A thesis submitted to attain the degree of

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(Dr. sc. ETH Zurich)

presented by

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Abstract

In this thesis, the solar-thermochemical splitting of H$_2$O and CO$_2$ to produce H$_2$ and CO (syngas) via ceria redox reactions is investigated experimentally within lab-scale solar reactors. In the first, high-temperature solar endothermic reduction step at $>1400$ °C, ceria is partially reduced to a non-stoichiometric state. In the subsequent low-temperature exothermic oxidation step at $<1400$ °C, the reduced ceria is oxidized with H$_2$O and/or CO$_2$ to generate H$_2$ and/or CO. Syngas can be further processed to conventional liquid transportation fuels via mature catalytic fuel synthesis processes. The key performance indicator of the solar reactor is the solar-to-fuel energy conversion efficiency, defined as the ratio of the heating value of the H$_2$ and/or CO produced to the input of solar radiative energy and the energy penalties associated to inert gas separation and vacuum pumping.

A simple cavity receiver-reactor prototype has been tested previously (gen-1 reactor). In this work, the syngas throughput and the solar-to-fuel energy conversion efficiency are improved by three main steps. First, an improved material structure is tested using the existing gen-1 reactor to enhance the throughput. Second, an improved 2$^{nd}$ generation solar reactor is designed, manufactured and experimentally tested (gen-2 reactor). Third, vacuum operation during the thermal reduction step is investigated within the gen-2 reactor to further boost the fuel yield and the efficiency.

The highest efficiency with the gen-1 reactor was obtained previously using a reticulated porous ceramic (RPC) foam structure made of pure ceria. It enabled a high reactor mass loading and efficient absorption of concentrated solar radiation, but had a low surface area which impeded the oxidation reaction. To improve the oxidation rates, a novel RPC structure with dual-scale porosities (DS-RPC) is tested in the solar reactor. It features mm-size pores for volumetric radiation absorption during reduction and µm-size pores within its struts for
enhanced oxidation rates. During the reduction step at 1450-1600 °C, the DS-RPC is directly exposed to concentrated thermal radiation with power inputs ranging from 2.8-3.8 kW and mean solar flux concentration ratios at the reactor aperture of up to 3000 suns. In the subsequent oxidation step, ceria is re-oxidized with CO$_2$ and/or H$_2$O at 700-1200 °C. In total more than 290 redox cycles performed over 210 hours are presented using the DS-RPC structure. Oxidation rates are twice as high as reported with the previously tested single-scale RPC and largely stable over time, increasing the fuel throughput per mass of ceria by 78 %. Ultimately, the total cycle time is 25 min and the solar-to-fuel energy conversion efficiency is 1.72 %. The syngas produced during 243 solar reactor cycles is collected and compressed to 150 bars, yielding 700 standard liters of syngas of composition 33.7 % H$_2$, 19.2 % CO, 30.5 % CO$_2$, 0.06 % O$_2$, 0.09 % CH$_4$, and 16.5 % Ar. The syngas is further processed via FT-synthesis within the European consortium SOLARJET to demonstrate for the first time the entire production chain to renewable kerosene via solar thermochemical splitting of H$_2$O and CO$_2$.

The results of the first reactor prototype reveal a great optimization potential in terms of geometrical design and flow configuration. Therefore, a second generation 4 kW solar reactor is designed, fabricated, and tested experimentally at ETH’s high-flux solar simulator. It consists of a windowed cavity-receiver containing the DS-RPC structure made of ceria, which is directly exposed to concentrated solar radiation. Monte-Carlo ray tracing and CFD simulations are applied to determine the cavity geometry to reach uniformity in the radiative flux over the RPC surface and fluid flow across the RPC. The hollow struts of the DS-RPC structure are infiltrated to improve the mechanical stability and porosity. Experimentation is carried out with varying radiative power input (2.4-4.1 kW), reduction temperature (1450 °C-1550 °C), purge Ar gas flow rate during reduction (4-13 L min$^{-1}$), oxidation temperature (750-1200 °C), and H$_2$O/CO$_2$ flow rate during oxidation (1-7 L min$^{-1}$). The reduction temperature is found to have a strong influence on the solar-
to-fuel energy conversion efficiency, with higher temperatures being beneficial within the considered range. Thermodynamic calculations reveal that the CO\textsubscript{2} conversion during oxidation at above 1000 °C is close to the thermodynamic limit. Upon optimization of the operating parameters, the solar-to-fuel energy conversion efficiency for splitting CO\textsubscript{2} into separate streams of CO and O\textsubscript{2} is increased by 50 % compared to the gen-1 reactor and reaches a value of 2.6 %.

For further efficiency improvement, combined vacuum-temperature swing operation of the gen-2 solar reactor is investigated experimentally. During the reduction step, the reactor is evacuated to pressures in the range 100-10 mbar while heated to the reduction temperature whereas subsequent oxidation with CO\textsubscript{2} to produce CO is performed at atmospheric pressure. Vacuum operation reveals multiple benefits on the reactor performance. The reduction time duration is shortened by 13 % due to decreased heat losses. The fuel yield at 10 mbar is 73 % higher compared to inert-swept atmospheric pressure operation due to a 10-fold lower oxygen partial pressure. The solar-to-fuel energy conversion efficiency during vacuum operation at optimized conditions is two times greater compared to ambient pressure operation and reaches a value of 5.25 %.
Zusammenfassung

In der vorliegenden Arbeit wird das solar-thermochemische Spalten von H₂O und CO₂ zur Herstellung von H₂ und CO (Synthesegas) basierend auf Ceridioxid Redoxreaktionen experimentell in Labor-Solarreaktoren untersucht. Im ersten endothermen Prozessschritt bei hohen Temperaturen (>1400 °C) wird das Ceridioxid partiell reduziert. Im darauffolgenden zweiten Schritt wird das Ceridioxid bei tieferen Temperaturen (<1400 °C) mit H₂O und/oder CO₂ wieder oxidiert um H₂ und/oder CO herzustellen. Synthesegas kann mittels etablierten katalytischen Syntheseverfahren zu konventionellen flüssigen Treibstoffen weiterverarbeitet werden. Der wichtigste Indikator für die Leistung des Reaktors ist der energetische Umwandlungswirkungsgrad von Sonnenenergie zu chemischer Energie. Er ist definiert als das Verhältnis vom Brennwert des produzierten Wasserstoffs und/oder Kohlenmonoxids dividiert durch die benötigte Solarenergie sowie zusätzliche Energieeinträge wie z.B. die Energie die benötigt wird um das Inertgas zu separieren oder die Vakuumpumpe zu betreiben.

Im Vorfeld zu dieser Arbeit wurde bereits ein einfacher Kavitätsreaktor gebaut und getestet (Gen-1 Reaktor). In dieser Arbeit werden der Synthesegasdurchsatz und der Reaktorwirkungsgrad in drei Schritten verbessert. Zuerst wird eine verbesserte Materialstruktur im Gen-1 Reaktor getestet um den Durchsatz zu verbessern. In einem zweiten Schritt wird ein verbesserter Solarreaktor entwickelt, gebaut und experimentell getestet (Gen-2 Reaktor). Im dritten Schritt wird der Betrieb unter Vakuum während dem thermischen Reduktionsschritt im Gen-2 Reaktor experimentell untersucht.

Der höchste Wirkungsgrad mit dem Gen-1 Reaktor wurde im Vorfeld mit einer netzartigen porösen Schaumstruktur (RPC) aus purem Ceridioxid erreicht. Diese hatte gute Strahlungseigenschaften da die
Zusammenfassung

Strahlung volumetrisch absorbiert wurde und ermöglichte eine hohe Massenbeladung im Reaktor aufgrund seiner tiefen Porosität, allerdings war die spezifische Oberfläche sehr klein was zu langsamen Oxidationsraten führte. Um diese zu erhöhen wird eine neuartige RPC Struktur mit Poren auf zwei Größenskalen im Solarreaktor getestet. Die Struktur hat Poren im mm-Bereich um die einfallende Strahlung volumetrisch zu absorbieren, und kleinere Poren im µm-Bereich um die spezifische Oberfläche und damit die Oxidationsraten zu erhöhen (DS-RPC). Während dem Reduktionsschritt bei 1450-1600 °C wird der DS-RPC direkt konzentrierter Wärmestrahlung mit Solarleistungen im Bereich 2.8-3.8 kW und einer thermischen Strahlungsdichte gemittelt über die Reaktorapertur von bis zu 3000 kW m⁻² (3000 Sonnen) ausgesetzt. Im darauffolgenden Oxidationsschritt wird das Cerdiooxid mit CO₂ und/oder H₂O bei 700-1200 °C oxidiert. Insgesamt werden mehr als 290 Redox-zyklen über 210 Betriebsstunden mit der DS-RPC Struktur präsentiert. Die Oxidationsraten sind doppelt so hoch wie mit der vorrangig getesteten RPC Struktur ohne µm-Poren und sie sind grösstenteils stabil über die Zyklen, wobei der Treibstoffdurchsatz pro Masse Cerdiooxid um 78 % höher ist. Die Zyklenzeit von optimierten Zyklen ist 25 Minuten und der energetische Wirkungsgrad 1.72 %. Während 243 Zyklen wird das Synthesegas gesammelt und auf 150 bar komprimiert, so dass insgesamt 700 Standardliter Synthesegas mit folgender Zusammensetzung gespeichert werden: 33.7 % H₂, 19.2 % CO, 30.5 % CO₂, 0.06 % O₂, 0.09 % CH₄, und 16.5 % Ar. Im Rahmen des EU-Projekts SOLARJET wird dieses Synthesegas mittels Fischer-Tropsch Synthese weiterverarbeitet um erstmals die gesamte Prozesskette zu erneuerbarem Kerosin mittels solar-thermochemischer Spaltung von H₂O und CO₂ zu demonstrieren.

Die Ergebnisse vom ersten Reaktorprototyp zeigen grosses Verbesserungspotential im geometrischen Design und in der Strömungskonfiguration auf. Deshalb wird ein weiterentwickelter 4 kW Gen-2 Solarreaktor entworfen, gebaut und experimentell im Hochfluss-Sonnensimulator der ETH getestet. Er besteht aus einem
Kavitätsreaktor mit Quarzfenster, in welchem die DS-RPC Struktur direkt bestrahlt wird. Monte-Carlo Strahlungs Simulationen und CFD Simulationen werden verwendet um eine gleichmässige Strahlungsdichte auf der Cerdioxid-Struktur und ein gutes Strömungsfeld zu erreichen. Die Experimente werden mit variierender Solarleistung (2.4-4.1 kW), Reduktionstemperatur (1450-1550 °C), Ar Durchfluss (4-13 L min⁻¹), Oxidationstemperatur (750-1200 °C) und H₂O/CO₂ Durchfluss (1-7 L min⁻¹) durchgeführt. Der energetische Wirkungsgrad zeigt eine starke Abhängigkeit von der verwendeten Reduktionstemperatur, wobei höhere Temperaturen im untersuchten Bereich zu besseren Wirkungsgraden führen. Thermodynamische Berechnungen zeigen das die experimentell gemessene CO₂ zu CO Umwandlung bei Oxidationstemperaturen >1000 °C nahe dem thermodynamischen Limit liegt. Mit optimierten Bedingungen liegt der energetische Wirkungsgrad zur Spaltung von CO₂ um 50 % höher als mit dem Gen-1 Reaktor und erreicht einen Wert von 2.6%.

Um den Wirkungsgrad weiter zu erhöhen wird der Betrieb unter Vakuum während der Reduktion im Gen-2 Reaktor experimentell untersucht. Während der Reduktion wird der Reaktor zu Drücken im Bereich 100-10 mbar evakuiert während er zu der gewünschten Reduktionstemperatur aufgeheizt wird. Die darauffolgende Oxidation mit CO₂ wird bei atmosphärischem Druck durchgeführt. Der Betrieb unter Vakuum zeigt mehrere Vorteile, so ist zum Beispiel die Reduktionstemperatur aufgrund von tieferen Wärmeverlusten um 13 % verkürzt. Der Treibstoffertrag pro Zyklus ist um 73% höher unter Vakuum (10 mbar) im Vergleich zu atmosphärischem Druck mit Inertgas Spülung aufgrund eines 10-fach verringerten Sauerstoff-Partialdrucks während der Reduktion. Der energetische Wirkungsgrad ist zweimal so gross ist wie bei atmosphärischem Betrieb, und erreichte einen Wert von 5.25 %.
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**Nomenclature**

\( A_{\text{aperture}} \) aperture surface area
\( A_{fs} \) fluid-solid area density
\( C \) solar flux concentration ratio
\( E_{\text{inert}} \) energy required for inert gas separation
\( g \) gravitational acceleration
\( h \) enthalpy
\( h_{fs} \) interphaseal heat transfer coefficient
\( I \) direct normal solar irradiation
\( \bar{I} \) identity matrix
\( K_f \) equilibrium constant
\( \bar{K} \) isotropic porosity tensor
\( k \) thermal conductivity
\( m_{\text{CeO}_2} \) ceria RPC reactor mass loading
\( p \) absolute pressure
\( p_{O_2} \) oxygen partial pressure
\( P_{\text{Solar}} \) solar radiative power input
\( Q_{\text{fuel}} \) energy contained in fuel produced
\( Q_{\text{inert}} \) heat equivalent required for inert gas separation
\( Q_{\text{pump}} \) heat equivalent of work required for vacuum pumping
\( Q_{\text{solar}} \) integrated solar energy input to the cycle
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{S}_M$</td>
<td>momentum source</td>
</tr>
<tr>
<td>$\bar{S}_{M, \text{buoy}}$</td>
<td>buoyancy momentum loss vector</td>
</tr>
<tr>
<td>$\bar{S}_{M, \text{porous}}$</td>
<td>porous momentum loss vector</td>
</tr>
<tr>
<td>$r$</td>
<td>molar flow rate</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time duration</td>
</tr>
<tr>
<td>$T_{\text{end oxidation}}$</td>
<td>temperature at the end of the oxidation step</td>
</tr>
<tr>
<td>$T_{\text{reduction}}$</td>
<td>temperature at the end of the reduction step</td>
</tr>
<tr>
<td>$T_{\text{start oxidation}}$</td>
<td>temperature at beginning of the oxidation step</td>
</tr>
<tr>
<td>$\vec{U}$</td>
<td>velocity vector</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>volumetric flow rate (at 273.15 K and 1 atm)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>nonstoichiometry</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>porosity</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>surface emittance</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>heating value</td>
</tr>
<tr>
<td>$\eta_{\text{absorption}}$</td>
<td>solar absorption efficiency</td>
</tr>
<tr>
<td>$\eta_{\text{heat-to-work}}$</td>
<td>heat-to-work energy conversion efficiency</td>
</tr>
<tr>
<td>$\eta_{\text{pump}}$</td>
<td>vacuum pump efficiency</td>
</tr>
<tr>
<td>$\eta_{\text{solar-to-fuel}}$</td>
<td>solar-to-fuel energy conversion efficiency</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity</td>
</tr>
</tbody>
</table>
**Abbreviations**

CCD  charge-coupled device  
CCS  carbon capture and storage  
CFD  computational fluid dynamics  
CPC  compound parabolic concentrator  
CPR2  cascading pressure receiver reactor  
CR5  counter rotating ring receiver reactor recuperator  
CSP  concentrated solar power  
DS-RPC  dual-scale reticulated porous ceramic  
ETH  Swiss Federal Institute of Technology  
FP7  Seventh Framework Programme for Research and Technological Development  
FT  Fischer-Tropsch  
HFSS  high flux solar simulator  
L  standard liters (at 273.15 K and 1 atm)  
LOD  lower limit of detection  
MC  Monte-Carlo  
PPB  parts per billion  
ppi  pores per inch  
PSI  Paul Scherrer Institute  
PTR-MS  proton transfer reaction-mass spectrometry  
PV  photovoltaic
RPC  reticulated porous ceramic
RWGS  reverse water-gas-shift
SEM  scanning electron microscopy
SOLAR-JET  solar chemical reactor demonstration and optimization for long-term availability of renewable jet fuel
SS-RPC  single-scale reticulated porous ceramic
TGA  thermogravimetric analysis
WGS  water-gas-shift
Chapter 1

Introduction

The transition away from fossil fuels as main primary energy source is inevitable for ensuring stable long-term energy supply and for limiting global warming to an acceptable level.\textsuperscript{1} The most abundant renewable energy source is solar energy with the energy incident on only 0.8\% of the Sahara desert’s surface being equal to the world’s primary energy demand. 8\% of the Sahara would therefore be sufficient to meet the total global energy demand assuming that solar energy could be converted to useful energy at 10\% efficiency.\textsuperscript{2} However, the uneven distribution of solar energy across the globe, the dilute flux hitting the earth’s surface and the intermittent occurrence render its technical use economically challenging. While the conversion of solar energy to electricity is already applied commercially,\textsuperscript{3} its conversion to storable and transportable liquid fuels requires further technology improvements.\textsuperscript{4} Transportation accounts for 64\% of the global oil consumption,\textsuperscript{2} and it is the sector where a transition away from liquid hydrocarbon fuels is especially difficult. While short-distance passenger transport could be readily met with battery electric vehicles, other transportation sectors such as aviation, truck-based transportation or long distance car travel require high energy density fuels. Renewably drop-in fuels that can be added to the current fuel mix are an ideal substitute for fossil-based fuels as no change in car and aircraft fleet or in distribution infrastructure is required.

An intermediate product in the production chain of such fuels is syngas, a mixture of H\textsubscript{2} and CO. It can be produced from the
combustion products CO₂ and H₂O via various processes by using solar radiation to provide the required energy input. Syngas is further processed to liquid hydrocarbon fuels via Fischer-Tropsch or other catalytic processes.⁵ If CO₂ is captured from atmospheric air the cycle offers a closed carbon loop and net CO₂ release results only from construction and operation of the equipment involved,⁶ as schematically indicated in Figure 1.1.

![Figure 1.1. Process scheme of producing liquid hydrocarbon fuels from concentrated sunlight, water and carbon dioxide. If carbon dioxide is captured from ambient air, the process is in general CO₂-neutral.](image)

The greatest challenge is the efficient conversion of solar energy to chemical energy in the form of syngas. Even though solar energy is readily available, its concentration requires expensive, large surface area collection infrastructure which typically represents the main cost driver of applications involving concentrated solar energy. Therefore, the efficient conversion of solar radiation to chemical fuels is crucial to decrease their cost.⁷

There exist various approaches to produce liquid fuels from solar energy. The direct way to split H₂O and CO₂ is thermal decomposition, but this route is not considered technically feasible due to the very high temperatures required (T>2800 °C for 10 % H₂)⁸ and the need for
high temperature gas separation or rapid quenching to avoid recombination. Alternative paths include biofuels that are produced from growing biomass and processing to liquid biofuels,\textsuperscript{9-10} Photocatalytic water-splitting,\textsuperscript{11-12} water electrolysis driven with PV or CSP electricity\textsuperscript{13-14} and photo-electrochemical cells.\textsuperscript{15-18} If hydrogen is produced, additional steps need to be considered for the conversion of H\textsubscript{2} to liquid hydrocarbons.

In this thesis the solar-thermochemical splitting of H\textsubscript{2}O and CO\textsubscript{2} using metal oxide redox reactions is considered. This production pathway is in a rather early stage of research but offers high thermodynamic efficiencies, allows for the direct production of syngas, and does not compete with food production as uncultivable land can be used.

1.1 Solar Thermochemical H\textsubscript{2}O and CO\textsubscript{2} Splitting Using Metal Oxide Redox Reactions

Two-step solar thermochemical splitting of H\textsubscript{2}O and CO\textsubscript{2} via metal oxide redox reactions can be represented by:\textsuperscript{19}

1\textsuperscript{st} step: high temperature solar endothermic reduction of a metal oxide:

\[
\text{MO}_{\text{ox}} \rightarrow \text{MO}_{\text{red}} + \frac{1}{2}\text{O}_2 \quad (1.1)
\]

2\textsuperscript{nd} step - oxidation with CO\textsubscript{2}:

\[
\text{MO}_{\text{red}} + \text{CO}_2 \rightarrow \text{MO}_{\text{ox}} + \text{CO} \quad (1.2)
\]

Oxidation with H\textsubscript{2}O:

\[
\text{MO}_{\text{red}} + \text{H}_2\text{O} \rightarrow \text{MO}_{\text{ox}} + \text{H}_2 \quad (1.3)
\]

Where MO\textsubscript{ox} and MO\textsubscript{red} denote the oxidized and reduced states of a metal oxide, respectively. In the first step, the metal oxide is reduced using concentrated solar energy as the heat input to provide the
enthalpy of the reaction. This step is thermodynamically favored at high temperatures and low oxygen partial pressures. Low \( p_{O_2} \) is typically accomplished by using an inert purge gas to dilute/sweep the released oxygen or by lowering the total pressure. In the second oxidation step that is thermodynamically favored at lower \( T \), the reduced metal oxide is oxidized back to the initial state with \( H_2O \) and \( CO_2 \) to produce \( H_2 \) and \( CO \). The metal oxide can then be recycled back to the first reduction step.\(^{20}\)

Dividing the \( H_2O \) and \( CO_2 \) dissociation reactions into two steps offers several advantages. The maximum required process temperature is typically much lower compared to direct thermolysis. Furthermore, fuel and oxygen are released in separate steps, avoiding high temperature gas separation or quenching.

The key performance indicator of this process is the solar-to-fuel energy conversion efficiency, defined as the ratio of the heating value of the fuel produced to the input of solar energy and all energy penalties associated with the production of the fuel:

\[
\eta_{\text{solar-to-fuel}} = \frac{Q_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{penalties}}} \tag{1.4}
\]

Where \( Q_{\text{fuel}} \) is the heating value of the \( H_2 \) and \( CO \) produced, \( Q_{\text{solar}} \) is the solar energy input and \( Q_{\text{penalties}} \) contains all energy penalties associated with the process, such as inert gas separation or vacuum pumping.

Various metal oxides have been considered for two-step thermochemical \( H_2O/CO_2 \) splitting. One class of materials sublimes upon reduction such as the \( Zn/ZnO \) cycle\(^ {21-22} \) and the \( SnO/SnO_2 \) cycle.\(^ {23} \) They offer high thermodynamic efficiencies thanks to high fuel yields per mass of metal oxide. Because of the sublimation of the metal, the resulting mixture of oxygen and gaseous metal or metal oxide requires rapid quenching to avoid recombination, which is technically challenging and causes a significant energy penalty. While
the thermodynamic efficiency of the zinc cycle without heat recovery is 39 % for CO₂ splitting at 1727 °C without heat recovery,²⁴ the experimentally demonstrated values using a 100 kW solar reactor were very low (>0.2 %), partly because of the excessive energy penalty for quenching.²⁵

The ferrite cycle using the FeO/Fe₃O₄ redox pair was the first two step metal-oxide cycle studied in 1977 by Nakamura,²⁶ but requires high temperatures above 2000 K that cause liquefaction and partial vaporization of the material which render the cycle technically uninteresting.²⁷ The required temperatures can be lowered by replacing a fraction of the iron oxide with other metals such as Mn, Ni, Zn or Co (mixed-metal ferrites) and the material can be stabilized using inert supports such as zirconia, yttria-stabilized zirconia, alumina or silicone oxide, however care has to be taken to avoid side-reactions between the materials.²⁸-³⁴

In contrast to these materials that react stoichiometrically, another class of materials releases only a small fraction of the oxygen contained in the lattice and is thereby reduced to a nonstoichiometric state. This enables more stable material structures as phase transitions can be avoided and quenching is not required as the metal oxide remains solid. The main drawback is the smaller fuel yield per mass of material that increases the energy penalty for cyclic heating and cooling of the metal oxide in a temperature-swing process if the sensible heat is not recovered.²⁰ One promising nonstoichiometric material class are perovskite oxides with the general structure ABO₃, where A and B denote metal cations.³⁵-³⁷ These materials can be doped on both the A and B sites, enabling many possible material compositions. One promising candidate composition is LaAlO₃ doped with Mn on the A and Sr on the B side, respectively, that shows high reduction extents at moderate temperatures.³⁸ However the oxidation with H₂O/CO₂ requires low oxidation temperatures and/or large oxidant excess.³⁹ To compare the expected process efficiencies using different materials, it is therefore not sufficient to compare the oxygen
release capacity, but requires an efficiency analysis that includes all relevant energy penalties.\textsuperscript{40}

1.2 The Ceria Cycle

Among the non-volatile metal oxides, non-stoichiometric cerium dioxide (ceria, CeO\textsubscript{2-\(\delta\)}) has emerged as a promising redox material because it offers morphological and crystallographic stability during redox cycling and fast redox kinetics due to its high O\textsuperscript{2-} conductivity.\textsuperscript{41-42} Cerium is a rare-earth metal with similar abundance in the earth’s crust as copper.\textsuperscript{43} The two-step H\textsubscript{2}O/CO\textsubscript{2} splitting cycle via ceria redox reactions is represented by:

**reduction:**

\[
\text{CeO}_2 \rightarrow \text{CeO}_{2-\delta} + \frac{\delta}{2}\text{O}_2 \tag{1.5}
\]

**oxidation with H\textsubscript{2}O:**

\[
\text{CeO}_{2-\delta} + \delta\text{H}_2\text{O} \rightarrow \text{CeO}_2 + \delta\text{H}_2 \tag{1.6}
\]

**oxidation with CO\textsubscript{2}:**

\[
\text{CeO}_{2-\delta} + \delta\text{CO}_2 \rightarrow \text{CeO}_2 + \delta\text{CO} \tag{1.7}
\]

In the endothermic solar reduction step (Equation 1.5), typically performed at $T_{\text{reduction}} > 1400$ °C, ceria is partially reduced to a non-stoichiometric state defined by $\delta$. In the exothermic oxidation step (Equations 1.6 and 1.7), typically performed at $T_{\text{oxidation}} < 1400$ °C, ceria is oxidized with H\textsubscript{2}O and/or CO\textsubscript{2} to generate H\textsubscript{2} and/or CO. The net reactions are splitting of H\textsubscript{2}O and CO\textsubscript{2} into syngas and oxygen, which are released in different steps, and ceria is not consumed.

The process can be conducted either with a temperature and pressure swing or isothermally with only a pressure swing.\textsuperscript{44} Isothermal redox cycling avoids the need for recuperation of the sensible heat of the
solids but requires large amounts of inert gas and excess of oxidant
gas to compensate for the lower thermodynamic driving force when
redox cycling at constant temperature compared to the combined
pressure-temperature swing cycle.\textsuperscript{44-48}

\textbf{Ceria thermodynamics} - Pure stoichiometric cerium dioxide shows a
cubic fluorite crystal structure that persists from room temperature up
to the melting point at 2750 K.\textsuperscript{49} At elevated temperature and low \(p_{O_2}\),
ceria partially changes its oxidation state from Ce\textsuperscript{4+} to Ce\textsuperscript{3+}. The
resulting charge imbalances are compensated by oxygen vacancies
and the release of O\textsubscript{2}(g).\textsuperscript{49}

\textbf{Figure 1.2} shows the logarithm of the equilibrium non-stoichiometry
\(\delta\) versus the logarithm of the oxygen partial pressure at different
temperatures for pure ceria.\textsuperscript{50} At realistic conditions during reduction
in a solar reactor \((T = 1500 \, ^\circ C \text{ and } p_{O_2} = 10^{-3} \, \text{atm})\), a \(\delta\) of 0.023 was
measured which corresponds to an oxygen release of 1.5 mL \text{g}_{CeO_2}\textsuperscript{-1},
\textsuperscript{42} or 1.2 % of the O\textsubscript{2} contained in the material. An important behavior
of ceria is that high vacancy concentrations of up to \(\delta = 0.25\) can be
obtained without a change in crystal structure or phase (at sufficiently
high temperatures), which is essential to preserve a stable material
structure during cycling.\textsuperscript{42}

The oxidation reactions (Equations 1.6 and 1.7) are
thermodynamically favored when the equilibrium \(p_{O_2}\) of ceria (from
Figure 1.2) at given \(\delta\) and \(T\) is lower than the oxygen partial pressure
of the produced CO – CO\textsubscript{2} and H\textsubscript{2} – H\textsubscript{2}O gas mixture at the same
temperature which, for CO\textsubscript{2} splitting, is defined by:

\[
p_{O_2} = \left( \frac{K_f \cdot p_{CO_2}}{p_{CO}} \right)^2
\]  

(1.8)

Where \(K_f\) represents the equilibrium constant of the CO\textsubscript{2}
decomposition reaction. This calculation is under the assumption that
the CO\textsubscript{2}:CO molar ratio is not affected by direct thermal
decomposition of CO\textsubscript{2} which is valid because at \(T < 1200 \, ^\circ C\) the \(p_{CO}\)
from thermal decomposition of pure CO$_2$ is about 2 orders of magnitude lower than from CO$_2$ reduction on ceria.

This has direct implications on the process. The maximum attainable conversion of CO$_2$ to CO and H$_2$O to H$_2$ is limited by thermodynamics and increases towards higher $\delta$ and lower oxidation temperature. For example: at $\delta = 0.025$ and $T_{\text{oxidation}} = 1200$ °C the maximum attainable CO concentration is 5.5 %, whereas at $T_{\text{oxidation}} = 800$ °C and same $\delta$ it is 89 %. Furthermore, full oxidation of ceria to $\delta = 0$ can only be achieved with high excess of oxidants.

These findings imply a trade-off on the operating conditions because a high oxidation temperature is desired for a low temperature swing between reduction and oxidation, but low temperatures are required to achieve high syngas concentrations. Complete oxidation is desired for high fuel yield but again results in low conversion.

Figure 1.2. Equilibrium oxygen nonstoichiometry of ceria versus oxygen partial pressure for different temperatures.$^{50}$
A high selectivity towards H\textsubscript{2} and CO is desired if liquid fuel synthesis is targeted. For the oxidation of 15 % samarium doped ceria with H\textsubscript{2}O and CO\textsubscript{2} at 650 °C, thermodynamics predict that 89 % of the carbon is present as solid carbon (graphite) and at lower temperatures the formation of methane is predicted, but it is not observed experimentally.\textsuperscript{41-51} Even at low temperatures in the range 400 - 700 °C, full selectivity towards CO and H\textsubscript{2} are observed experimentally which is explained by kinetics rather than thermodynamics. Direct production of methane can be accomplished when ceria is coated with Ni as catalyst.\textsuperscript{41}

For the catalytic synthesis of liquid fuels, the H\textsubscript{2}:CO molar ratio in the syngas should be in the range of 1.7 – 2 depending on the desired products and the catalysts used.\textsuperscript{5} Furler et al. showed that the composition can be adjusted by the molar feed ratio of H\textsubscript{2}O:CO\textsubscript{2}.\textsuperscript{52} Figure 1.3 shows the syngas composition as function of the H\textsubscript{2}O:CO\textsubscript{2} molar ratio in the reactant gas. The reactant and product molar ratios showed a linear correlation and H\textsubscript{2}:CO molar ratios in the range 0.25 to 2.34 were obtained experimentally. The H\textsubscript{2}:CO ratio decreased for increasing temperatures which is assumed to be due to the reverse water gas shift reaction that is favorable at high temperatures, and because the CO\textsubscript{2} reduction is thermodynamically favored compared to H\textsubscript{2}O reduction at increasing temperatures.\textsuperscript{51}

Reported theoretic energy conversion efficiencies of the ceria cycle vary widely from 7.5 to beyond 30 %.\textsuperscript{44-45, 53-56} The results depend strongly on the assumptions made, especially for heat recovery, re-radiation losses, reduction/oxidation temperatures, the flow field that dictates the required amount of inert gas (for example closed system, plug flow or counter flow) or vacuum pump efficiencies when considering operation at reduced pressure.\textsuperscript{57}
Figure 1.3. Syngas composition as function of H$_2$O:CO$_2$ molar reactant feed ratio.$^{51}$

The thermodynamic properties of ceria can be tailored by introducing dopant elements.$^{58-62}$ Scheffe et al. $^{54}$ showed, that doping with Gd, Y, Sm, Ca and Sr decreases the equilibrium non-stoichiometry for a given temperature and oxygen partial pressure. Furthermore, also the reduction enthalpy is decreased and a lower thermodynamic efficiency is expected for these dopants. Other dopants such as Zr$^{63}$ can lower the reduction temperatures, however the required temperature swing between reduction and oxidation increases because lower temperatures are necessary to oxidize the material.$^{40, 64}$ Also Cr,$^{65}$ Mn, Fe, Ni and Cu$^{58}$ were shown to lower the reduction temperatures for constant $\delta$.

**Reduction kinetics** - Oxygen bulk diffusion in ceria is reported to be exceptionally rapid.$^{41-42, 66}$ During thermal reduction (Equation 1.5), oxygen diffuses through the bulk to the surface where it is released as molecular oxygen to the gas phase. An estimation of the diffusion time scale$^{42}$ and experimental results$^{67}$ indicate that the ceria reduction (with all involved serial steps) occur rapidly enough such the material
nonstoichiometry follows the thermodynamic equilibrium at relevant solar reactor conditions. Hence, the O₂ release rate obtained in a solar reactor is dictated by the heating rate and the rate of oxygen removal rather than kinetics, therefore efficient heat and mass transfer to the material are important to improve this reaction step.

**Oxidation kinetics** - Chueh *et al.*⁴² investigated the oxidation reaction of 15% Samarium-doped ceria and found reaction orders for CO₂ and H₂O splitting of 0.77 and 0.54, respectively, indicating a surface reaction limited process (assuming a power rate law for the CO₂ and H₂O concentration).⁴¹ This was confirmed by the observation that the rates strongly increased upon coating the surface with Rh as catalyst. The results are in good agreement with results obtained with pure ceria using porous structures with different porosities where the oxidation rates scaled with the specific surface area.⁶⁸ Therefore, it can be concluded that the fuel production rates achieved in a solar reactor depend on the specific surface area of the ceria structure used (as long as thermodynamic and external mass transfer limitations can be excluded).

**Material structures** - Efficient heat transfer of concentrated solar radiation and rapid chemical reactions are desired characteristics for the two-step thermochemical cycle.⁶⁹ A directly irradiated redox material structure needs to fulfill three morphological properties in order to meet these characteristics:

- high volumetric mass (low porosity) for a high ceria mass loading in the reactor for high fuel yield per cycle
- good light penetration (low optical thickness) for an efficient volumetric absorption of incident radiation and homogeneous temperature across the structure during transient heating
- high specific surface area for rapid oxidation reactions

Various candidate material structures for solar reactors that use direct absorption of concentrated solar radiation coupled with surface
chemical reactions have been examined. Structures investigated include lattice type structures,\textsuperscript{69-70} porous monolithic structures,\textsuperscript{71} vertical pins,\textsuperscript{70} honeycombs\textsuperscript{72} and foam structures.\textsuperscript{67,73-75}

Often, the redox material is coated on an inert support such as zirconia, alumina or silicon carbide which can lead to structural problems\textsuperscript{74} and side reactions with the support.\textsuperscript{72-73} Also, the support represents an inert thermal mass that needs to undergo temperature cycling without contributing to the fuel production.\textsuperscript{42,74}

Different structures made of pure ceria have been investigated in a simple solar cavity receiver-reactor, namely a monolithic brick structure\textsuperscript{71}, a felt structure\textsuperscript{52} and a reticulated porous ceramic (RPC) structure\textsuperscript{67}. The monolithic brick and the felt structures featured a high specific surface area but low mass and high optical thickness. Hence, while the oxidation step occurred rapidly, the reduction step was inefficient because radiation absorption was limited to the irradiated surface, causing high surface temperatures and temperature gradients across the structures. Poor fuel yields were obtained because of the high porosity, limiting the solar-to-fuel energy conversion efficiency to 0.15%. The performance was improved using a reticulated porous ceramic (RPC) foam type structure with pores in the mm-range ($d_{\text{mean}} = 2.5$ mm) to allow for volumetric absorption of the incoming radiation and much lower porosity, hence improving the heat transfer and fuel yield. The drawback was a low specific surface area which led to slow oxidation rates.

The structure was then further developed by introducing an additional porosity to the struts of the structure with a smaller void size ($d_{\text{mean}} = 10$ µm) in order to enhance the oxidation rates. Characterization of this dual-scale RPC (DS-RPC, with porous struts) by thermogravimetric analysis (TGA) resulted in up to tenfold CO$_2$ splitting rates than those obtained for the single-scale RPC with non-porous struts (SS-RPC).\textsuperscript{68}

**Solar reactor concepts** - Various reactor concepts for 2-step metal oxide cycles using stationary metal oxide structures,\textsuperscript{31,71,76-79} rotating
structures for recovering the sensible heat during thermal cycling, or moving particles have been proposed. Figure 1.4 shows selected reactor concepts that were experimentally tested; Figure 1.4 (a) depicts a schematic of the Counter Rotating Ring Receiver Reactor Recuperator (CR5) developed at Sandia National Laboratories. It consists of a set of counter-rotating rings coated with the active material. The rings are directly irradiated on one side for thermal reduction while they are oxidized on the opposite side with H$_2$O and/or CO$_2$. The sensible heat of the solids is recovered by radiation heat transfer between the counter-rotating discs. On-sun testing revealed promising performance but experimental difficulties arose due to cracking of the rotating structures and gas mixing between the reduction and oxidation zones. Figure 1.4 (b) shows a concept developed at the University of Minnesota that consists of a cavity receiver that is lined with Al$_2$O$_3$ tubes containing ceria pellets and is designed for isothermal operation. Outside of the reaction zone the tubes act as tube-in-tube heat exchanger to efficiently recover the sensible heat of the gases. Experimental testing revealed stable, reproducible and quasi-continuous operation by simultaneous reduction and oxidation in different tubes, but large quantities of inert gas and excess reactants were necessary to induce redox cycling under isothermal conditions, causing significant energy penalties. Figure 1.4 (c) shows a pilot-scale reactor developed at the Paul Scherrer Institute for the dissociation of ZnO particles that was tested on-sun in a 1 MW solar furnace in Odeillo, France. It features a rotating cavity receiver into which ZnO particles are fed and pressed against the reactor wall by centrifugal forces induced by the rotation. The particles simultaneously act as radiation absorber, insulation and reactant. The quenching of the produced Zn(g) and O$_2$(g) gas mixture to avoid recombination required excessive amounts of argon which limited the overall process performance.
Figure 1.4. (a) CR5 reactor featuring rotating reactive rings to recover the sensible heat.\textsuperscript{81} (b) Indirectly irradiated cavity receiver-reactor for isothermal operation.\textsuperscript{89} (c) Rotating cavity receiver-reactor for reduction of ZnO particles.\textsuperscript{27}
A recent concept developed in a collaboration between Sandia National Laboratories, German Aerospace Center, Arizona State University, Bucknell University, Colorado School of Mines and Stanford University, and led by Sandia National Laboratories, is the cascading pressure receiver reactor (CPR2) schematically depicted in Figure 1.5. The design is a further development of the initially patented moving bed design of Sandia National Laboratories.\(^{83, 88}\) Particles are reduced in multiple steps in different reduction chambers under direct irradiation and vacuum pressures. The different chambers are at successively lower vacuum pressures which has been shown to significantly decrease the required pumping speed and hence allows for lower pressure in the final chamber compared to using a single chamber.\(^{84}\) Vacuum seal between the different reduction chambers and to the oxidation zone is accomplished by packed beds of the metal oxide particles. Hydrogen is produced in a packed bed reaction chamber before the particles are elevated using a screw-type particle lifter and fed back to the first reduction chamber. The various components of the reactor are currently being tested.\(^{89-91}\)
Figure 1.5. Schematic of the CPR2 reactor. It features a particle elevator that feeds the redox material to multiple subsequent reduction chambers that are kept at successively lower pressures. After the last reduction chamber particles are fed to a packed bed oxidation chamber for H\textsubscript{2}O splitting. Pressure separation between the various chambers is achieved by packed beds of particles.\(^9\)

1.3 Thesis Goal and Outline

This thesis was performed within the framework of the European Union FP7 project SOLAR-JET (Solar chemical reactor demonstration and Optimization for Long-term Availability of Renewable JET fuel). Previous to this project, a solar reactor was developed in a joint collaboration between ETH Zurich, the California Institute of Technology and Paul Scherrer Institute (PSI).\(^7\) Figure 1.6 shows a schematic of the reactor prototype; it consists of a windowed cavity receiver that contains a directly irradiated, porous ceria structure. Within SOLAR-JET, this reactor has already been tested using various material structures.\(^5,6,7\)
Figure 1.6. Schematic of the solar reactor prototype for thermochemical splitting of H₂O and CO₂ via ceria redox reactions, containing a directly irradiated reticulated porous ceramic structure.⁶⁷

The best performance has been obtained using an RPC structure made of pure ceria at a solar power input of 3.8 kW. **Figure 1.7** shows the reactor temperature and O₂ and CO evolution rates of an optimized cycle that yielded a solar-to-fuel energy conversion efficiency of 1.7 %, which was 4 times higher than the next reported value for solar thermochemical CO₂ splitting at that time and represented the state-of-the-art at the beginning of this thesis.

Further goals of the SOLAR-JET project included the demonstration of the entire production chain from CO₂, H₂O and concentrated thermal radiation to kerosene, and the design, manufacturing and testing of an optimized solar reactor.

This thesis is structured in 3 main chapters. In each chapter, one key component of the process was modified with the goal of improving the fuel throughput and/or the solar-to-fuel energy conversion efficiency.
In the first chapter, a new material structure with increased specific surface area is tested in the solar reactor. This new structure helped to increase the throughput per mass of ceria by 78 %. The structure was tested over a large amount of cycles and the collected syngas was processed to the first-ever solar kerosene that was produced solely from concentrated simulated solar radiation, CO$_2$, and H$_2$O.

In the second chapter, the lessons learned from the operation of the first reactor prototype and from a numerical heat-and mass transfer model were used to design a second-generation (gen-2) solar reactor for improved thermal performance. The gen-2 reactor increased the energy conversion efficiency by 50 % compared to the initial design.

In the third chapter, a novel operation mode is investigated experimentally, namely the operation of the gen-2 solar reactor under vacuum pressure during reduction instead of operation at ambient pressure with inert gas sweeping. This new operating mode further increased the energy conversion efficiency by a factor of 2.
Chapter 2

Performance and Cycling of a Dual-Scale RPC Structure for Liquid Fuel Synthesis*

In this chapter, the cyclic performance of an existing 4 kW solar cavity-type reactor containing a recently developed dual-scale RPC structure is experimentally examined. The structure features dual-scale porosities: the larger void size, with $d_{\text{mean}} = 2.5 \text{ mm}$, enables volumetric absorption of concentrated solar radiation for efficient heat transfer to the reaction site during reduction, while the smaller void size within the struts, with $d_{\text{mean}} = 10 \mu\text{m}$, increases the specific surface area for enhanced reaction rates during oxidation with CO$_2$ and H$_2$O.

The stability of this structure and the cyclic performance of the solar reactor is evaluated by carrying out over 290 redox cycles under realistic operating conditions of direct high-flux irradiation and transient heat/mass transfer. The syngas-to-liquid process is experimentally demonstrated by compressing and storing of the produced syngas and its further processing via FT-synthesis to naphtha, kerosene and gasoil. The potential of this solar thermochemical path in terms of energy conversion efficiency vis-à-vis other alternative paths to renewable liquid fuels is briefly discussed.

2.1 Materials and Methods

**Materials** — Ceria RPC parts with dual-scale porosity were fabricated by the replication method. Cerium (IV)-oxide powder (particle size < 5 µm, 99.9% purity, Sigma Aldrich) was mixed with water in a 5:1 mass ratio, 30 Vol-% of spherical carbon pore-forming agent particles (particle size 0.4-12 µm, HTW Hochtemperatur-Werkstoffe GmbH), 0.83 wt-% organic deflocculating agent (Dolapix CE 64), polyvinyl alcohol binder (Optapix RA 4G), and antifoaming agent (Contraspum KWE), and processed according to a previously published recipe. Organic polyurethane sponges of 10 ppi (Foam-Partner, Fritz Nauer AG) were then immersed into the slurry, which was dried in air and finally sintered in an electrically heated furnace at 1600 °C. Figure 2.1 shows the DS-RPC with mm-sized pores (photograph) and µm-sized pores in its struts (inset, SEM micrograph).

![Figure 2.1](image-url)

**Figure 2.1.** Photograph of DS-RPC structure with visible mm-sized pores; the inset shows a SEM micrograph of a strut break plane with µm-sized pores.
**Experimental setup and methods** — A schematic and photographs of the experimental setup are shown in Figure 2.2 (a). It features the main system components of the production chain to solar kerosene from H$_2$O and CO$_2$ via the ceria-based thermochemical redox cycle. The key component is the solar reactor, shown schematically in Figure 2.2 (b). Its design was previously described,$^{51, 67-68, 71}$ the main features are briefly summarized here. It consisted of an insulated cavity-receiver with a 4 cm-diameter aperture to let in concentrated solar radiation. The reactor front was sealed by a 24 cm-diameter, 3 mm-thick clear fused quartz disk window. A compound parabolic concentrator (CPC$^{94}$) was incorporated onto the aperture to further boost the solar concentration ratio † to mean values of up to 3000 suns. The ceria RPC was contained within the cavity as a cylinder composed of four 20 mm-tick, 60 mm-i.d., 100 mm-o.d. rings, and a single 20 mm-thick, 100 mm-o.d. disk. The total mass of the CeO$_2$ cylinder was 948 g. Temperatures were measured at the outer surface of the RPC with B-type thermocouples. Reacting gases were injected through radial inlet ports and product gases exited through an outlet port at the rear plate. Argon (99.996% purity) and CO$_2$ (99.998% purity) flow rates were regulated by electronic mass flow controllers (Bronkhorst F-201 C). H$_2$O was delivered at 200°C by a steam generator (Bronkhorst F-201C) that was regulated by a liquid mass flow controller (Bronkhorst L2-FAC-11-0). Product gas composition was monitored by gas chromatography (Varian 490), supplemented by an electrochemical sensor for O$_2$ (Siemens Ultramat 23), infrared-based detectors for CO and CO$_2$ (Siemens Ultramat 23), and a thermal conductivity based detector for H$_2$ (Siemens Calomat 6).

† The solar concentration ratio $C$ is defined as $C = \frac{P_{\text{solar}}}{(I \cdot A)}$, where $P_{\text{solar}}$ is the solar radiative power intercepted by the aperture of area $A$, normalized to the direct normal solar irradiation $I$. $C$ is often expressed in units of “suns” when normalized to $I = 1 \text{ kW m}^{-2}$. 
Figure 2.2. (a) Schematic and photographs of the experimental setup, featuring the main system components of the production chain to solar kerosene from H₂O and CO₂ via the ceria-based thermochemical redox cycle. (b) Schematic of the solar reactor configuration. The cavity-receiver contains a reticulated porous ceramic (RPC) structure, made of ceria, with dual-scale porosity in the mm- and µm-scale.
Experimentation was performed at the High-Flux Solar Simulator (HFSS) of ETH Zurich. An array of seven Xe-arcs, close-coupled to truncated ellipsoidal reflectors, provided an external source of intense thermal radiation, mostly in the visible and IR spectra, that closely approximated the heat transfer characteristics of highly concentrating solar systems such as solar towers and dishes. The radiative flux distribution at the focal plane was measured optically using a calibrated CCD camera focused on a Lambertian (diffusely reflecting) target. The solar radiative power input through the aperture $P_{\text{solar}}$ was measured with a water calorimeter.

During a typical redox cycle, the reactor was heated by $P_{\text{solar}} = 2.8-3.8$ kW to the desired reduction temperature in the range 1450-1600 °C while purging with Ar flow rates $V_{\text{Ar}}$ ranging from 2 to 10 L min$^{-1}$. Following reduction, the HFSS was turned off ($P_{\text{solar}} = 0$) and the reactor was cooled to the desired oxidation temperature in the range 700-1200 °C. Subsequently, oxidation was performed at $P_{\text{solar}} = 0-0.8$ kW by injecting the reactant gases, either CO$_2$ or a mixture of CO$_2$ and H$_2$O. The product gas was collected in a gas sample bag (SKC series 263-50) and compressed to 150 bar.

The solar syngas collected was analyzed for catalyst poisons by proton-transfer-reaction mass spectrometry (PTR-MS) in the H$_3$O$^+$ mode at 600 V drift chamber voltage (Ionicon Analytik GmbH, Innsbruck, Austria). Electron micrographs were recorded on a Hitachi TM-1000 at an acceleration voltage of 15 kV. Mercury porosimetry was performed on a Quantachrome Poremaster 60-GT (Quantachrome GmbH + Co KG, Odelzhausen, Germany). Liquid fuel synthesis of the solar made syngas was performed via the Fischer-Tropsch using Co-based catalysts process at Shell Global Solutions, Amsterdam.
2.2 Results and Discussion

2.2.1 Cyclic Performance

The advantage of the novel RPC with dual-scale porosity (DS-RPC) vis-à-vis the previously tested RPC with single-scale porosity (SS-RPC, without strut porosity) is clearly seen when comparing experimental results using the same solar reactor under the same operating conditions. This type of comparison under realistic operating conditions of direct high-flux irradiation enables to elucidate the transient heat/mass transfer characteristics of both RPC structures. Figure 2.3 shows the nominal solar reactor temperature and O\textsubscript{2} and CO evolution rates during a CO\textsubscript{2}-splitting redox cycle obtained with the DS-RPC (solid lines; this study) and SS-RPC (dashed lines; previous study\textsuperscript{67}). A summary of the operating conditions and results are listed in Table 2.1.

![Figure 2.3](image)

**Figure 2.3.** Nominal solar reactor temperatures and O\textsubscript{2} and CO evolution rates during CO\textsubscript{2}-splitting redox cycles performed with the SS-RPC and DS-RPC under the same experimental conditions: $P_{\text{solar}} = 3.4$ kW with $V_{Ar} = 2$ L min\textsuperscript{-1} for 22 min during reduction; $P_{\text{solar}} = 0$ with $V_{CO2} = 2$ L min\textsuperscript{-1} + $V_{Ar} = 0.1$ L min\textsuperscript{-1} for 8 min during oxidation.
Table 2.1. Representative solar experimental conditions and results for a CO$_2$ splitting redox cycle using ceria RPC with dual-scale porosity (DS-RPC) and with single-scale porosity (SS-RPC, data from Ref. 67).

<table>
<thead>
<tr>
<th>Ceria structure</th>
<th>SS-RPC</th>
<th>DS-RPC$^{67}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria RPC mass (g)</td>
<td>1413</td>
<td>948</td>
</tr>
<tr>
<td>Solar radiative power input, $P_{solar}$ (kW)</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Reduction duration, $t_{reduction}$ (min)</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Ar flow rate reduction $V_{Ar}$ (L min$^{-1}$)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ flow rate during oxidation (L min$^{-1}$)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Reduction temperature, $T_{reduction}$ (°C)</td>
<td>1530</td>
<td>1547</td>
</tr>
<tr>
<td>Mean heating rate (°C min$^{-1}$)</td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>Peak heating rate (°C min$^{-1}$)</td>
<td>110</td>
<td>160</td>
</tr>
<tr>
<td>Non-stoichiometry, $\delta$</td>
<td>0.031</td>
<td>0.034</td>
</tr>
<tr>
<td>Peak specific O$_2$ evolution rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>0.16 ± 0.01</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>Total specific O$_2$ evolution (mL g$^{-1}$CeO$_2$)</td>
<td>2.01 ± 0.07</td>
<td>2.18 ± 0.05</td>
</tr>
<tr>
<td>Absolute O$_2$ evolution (L)</td>
<td>2.84 ± 0.10</td>
<td>2.07 ± 0.04</td>
</tr>
<tr>
<td>Peak specific CO release rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>0.37 ± 0.01</td>
<td>0.75 ± 0.04</td>
</tr>
<tr>
<td>Total specific CO release (mL g$^{-1}$CeO$_2$)</td>
<td>4.11 ± 0.12</td>
<td>4.41 ± 0.16</td>
</tr>
<tr>
<td>Absolute CO release (L)</td>
<td>5.80 ± 0.17</td>
<td>4.18 ± 0.15</td>
</tr>
<tr>
<td>Molar ratio CO:O$_2$</td>
<td>2.04 ± 0.14</td>
<td>2.02 ± 0.12</td>
</tr>
</tbody>
</table>
During the solar reduction step (Equation 1.5), both RPCs showed a similar behavior characterized by a rapid increase in ceria temperature (DS-RPC: peak rate of 160 °C min\(^{-1}\), SS-RPC: 110 °C min\(^{-1}\)) shortly after increasing the radiative power input from 0.8 to 3.4 kW, leading to peak temperatures of 1547 °C and 1530 °C for the DS-RPC and SS-RPC, respectively. The reduction rates were attributed to heat transfer limitations rather than chemical kinetics, as confirmed by comparing measured and equilibrium values of \(\delta\) as a function of \(p_{\text{O}_2}\) and \(T\).\(^{67}\)

However, because of the difference in sample masses (DS-RPC is 33% lighter than SS-RPC), \(\text{O}_2\) evolution from DS-RPC increased more rapidly initially compared to SS-RPC. \(\text{O}_2\) evolution began above 900 °C and reached a peak rate of 0.19 ± 0.02 mL min\(^{-1}\) g\(^{-1}\) CeO\(_2\) and 0.16 ± 0.01 mL min\(^{-1}\) g\(^{-1}\) CeO\(_2\) for the DS-RPC and SS-RPC, respectively. Total \(\text{O}_2\) yields for DS-RPC and SS-RPC were 2.18 ± 0.05 ml g\(^{-1}\) CeO\(_2\) (\(\delta = 0.034\)) and 2.01 ± 0.07 ml g\(^{-1}\) CeO\(_2\) (\(\delta = 0.031\)).

During the oxidation step with \(\text{CO}_2\) (Equation 1.7), the DS-RPC showed a considerably higher peak CO production rate of 0.75 ± 0.04 mL min\(^{-1}\) g\(^{-1}\) CeO\(_2\) compared to 0.37 ± 0.01 mL min\(^{-1}\) g\(^{-1}\) CeO\(_2\) measured for the SS-RPC. This is attributed to the interconnected µm-size pore network within the struts of the DS-RPC, which – as expected – significantly increased the reactive surface area from 0.000145 to 0.066 m\(^2\) g\(^{-1}\).\(^{67-68}\) In both cases, the ratio of fuel produced to oxygen released was approximately 2:1, implying that the oxygen non-stoichiometry was fully exploited for CO production and that the mass balance was closed.

The thermochemical performance of a solar reactor is given by the solar-to-fuel energy conversion efficiency \(\eta_{\text{solar-to-fuel}}\), defined as:

\[
\eta_{\text{solar-to-fuel}} = \frac{\Delta H_{\text{fuel}} \int r_{\text{fuel}} dt}{\int P_{\text{solar}} dt + E_{\text{inert}} \int r_{\text{inert}} dt}
\]  

(2.1)

where \(\Delta H_{\text{fuel}}\) is the higher heating value of the fuel produced, \(r_{\text{fuel}}\) is the molar rate of fuel produced, \(P_{\text{solar}}\) is the solar radiative power input
through the reactor aperture, $r_{\text{inert}}$ is the inert gas flow rate during reduction and $E_{\text{inert}}$ is the energy required for inert gas separation (assumed 20 kJ mol$^{-1}$). Note that $\eta_{\text{solar-to-fuel}}$ does not include the optical efficiency of the solar concentrating system, the losses occurring at the quartz window and at the secondary concentrator. Additionally, this definition assumes that only the high-temperature endothermic reduction step requires solar energy as an input. Note also that extending the duration of the reduction step for maximizing $O_2$ yield (and consequently $\delta$) does not necessarily maximize $\eta_{\text{solar-to-fuel}}$. This is because, during reduction, $P_{\text{solar}}$ is constant but $O_2$ evolution rate diminishes with time. The same applies to the duration of the oxidation step because heat is lost while CO evolution rate diminishes with time. Therefore, there are optimal time durations of the reduction and oxidation steps for which $\eta_{\text{solar-to-fuel}}$ is maximized. This can be elucidated from Figure 2.4 where the instantaneous $\eta_{\text{solar-to-fuel}}$ and the $O_2$ yield is plotted versus the reduction time (Figure 2.4 (a)) and instantaneous $\eta_{\text{solar-to-fuel}}$ and the CO yield versus oxidation time (Figure 2.4 (b)). In these experimental runs, the sensible heat carried by the hot gases exiting the solar reactor (Ar + $O_2$ during reduction; syngas and unreacted $H_2O/CO_2$ during oxidation) was not recovered. The sensible heat of solids lost during the temperature swing between reduction and oxidation steps was also not recovered. Recovering the sensible heat of both solids and gases can dramatically boost $\eta_{\text{solar-to-fuel}}$.\footnote{In this chapter, $P_{\text{solar}}$ does not include losses at the quartz window and the secondary concentrator.}
Figure 2.4. Instantaneous $\eta_{\text{solar-to-fuel}}$ and $O_2/CO$ yields versus reduction/oxidation reaction times.
Figure 2.5 shows the nominal reactor temperature and O\textsubscript{2} and CO evolution rates for two subsequent CO\textsubscript{2} splitting cycles at optimized reduction \((P_{\text{solar}} = 3.8 \text{ kW} \text{ and } \dot{V}_{\text{Ar}} = 6 \text{ L min}^{-1})\) and oxidation \((P_{\text{solar}} = 0 \text{ kW}, \dot{V}_{\text{Ar}} = 0.1 \text{ L min}^{-1}, \dot{V}_{\text{CO}_2} = 6 \text{ L min}^{-1})\). The optimal reduction and oxidation time durations were 15 min and 8 min, respectively, leading to an overall cycle duration of 25 min. Corresponding \(\eta_{\text{solar-to-fuel}}\) was 1.63 \% and 1.72 \% in the first and second cycles, respectively. These values are comparable to previously measured \(\eta_{\text{solar-to-fuel}}\) of 1.73 \% obtained with the SS-RPC\textsuperscript{67}, but the DS-RPC’s mass loading was 33 \% lower than that of the SS-RPC \((m_{\text{CeO}_2,\text{dual-scale}} = 948 \text{ g}, m_{\text{CeO}_2,\text{single-scale}} = 1413 \text{ g})\). Additionally, the cycle time was reduced from 37 min to 25 min.

**Figure 2.5.** Nominal solar reactor temperature and O\textsubscript{2} and CO evolution rates during 2 subsequent CO\textsubscript{2} splitting cycles at optimized reduction and oxidation times. Experimental conditions: \(P_{\text{solar}} = 3.8 \text{ kW with } \dot{V}_{\text{Ar}} = 6 \text{ L min}^{-1}\) for 15 min during reduction; \(P_{\text{solar}} = 0 \text{ with } \dot{V}_{\text{CO}_2} = 6 \text{ L min}^{-1} \text{ CO}_2 + \dot{V}_{\text{Ar}} = 0.1 \text{ L min}^{-1}\) for 8 min during oxidation.
In addition to $\eta_{\text{solar-to-fuel}}$, the utilization of the reacting material is of interest since the amount of redox material required to produce a certain amount of fuel could be a critical aspect of the process.$^{53}$ As a measure of this quantity a new indicator is introduced, $\bar{r}'_{\text{fuel}}$, defined as the mean specific fuel production rate:

$$\bar{r}'_{\text{fuel}} = \frac{\int r_{\text{fuel}} dt}{m_{\text{CeO}_2} t_{\text{cycle}}}$$

(2.2)

where $r_{\text{fuel}}$ is the fuel production rate (CO evolution rate in this case), $m_{\text{CeO}_2}$ is the ceria mass loading in the solar reactor, and $t_{\text{cycle}}$ is the duration of the cycle. $\bar{r}'_{\text{fuel}}$ becomes relevant as we compare the scalability of various reactor concepts, e.g. fixed redox structures vs. moving redox particles, pure redox materials vs. thin-films on inert supports. Based on the experimental data presented in Figure 2.5, $\bar{r}'_{\text{fuel}} = 13.1$ and 7.3 L$_{\text{fuel}}$ h$^{-1}$ kg$_{\text{CeO}_2}^{-1}$ for the DS- and SS-RPC, respectively. Thus, the strut porosity of the DS-RPC enhanced the utilization of the ceria by 78%. The improvement is even more significant when compared to the previously tested monolithic porous ceria structure (3.2 L$_{\text{fuel}}$ h$^{-1}$ kg$_{\text{CeO}_2}^{-1}$) and ceria felt (4.7 L$_{\text{fuel}}$ h$^{-1}$ kg$_{\text{CeO}_2}^{-1}$).$^{51, 71}$ We attribute the remarkable improvement to a trade-off between high surface area for enhanced oxidation rates, low overall porosity for high mass load of redox material, and low optical thickness for volumetric radiative absorption. The determination of the optimal pore sizes and porosities of the RPC is complex because of the coupled reaction kinetics and heat/mass transport properties, and requires solving numerically the Navier-Stokes conservation equations at the pore level using the exact 3D geometry obtained by micro-tomography.$^{97-99}$

Besides efficiency and material utilization, the cyclability of the redox material is essential. Chueh et al$^{71}$ performed 500 H$_2$O-splitting cycles in an IR furnace using a 0.4 g monolithic porous ceria sample and showed constant rates and overall production after an initial
The morphological stability of DS-RPC was recently investigated over 20 TGA consecutive cycles and a constant fuel production from cycle to cycle was observed, accompanied by a slight decrease in the peak rates due to grain growth. To assess the stability of the DS-RPC under realistic solar operating conditions of heat and mass transfer, multiple consecutive redox cycles were performed with the solar reactor. Figure 2.6 shows the nominal solar reactor temperature at the end of the reduction step and the peak CO and H₂ evolution rates for 291 redox cycles. The first 45 cycles (shown in Figure 2.6 region I and a close-up in Figure 2.7) were performed exclusively using CO₂ as an oxidant under varying experimental conditions (\( P_{\text{solar}} = 2.8-3.8 \) kW during reduction, \( P_{\text{solar}} = 0 \) kW during oxidation, and \( \dot{V}_{\text{Ar}} / \dot{V}_{\text{CO}_2} = 2-10 \) L min\(^{-1}\)), to examine the performance of the DS-RPC. The scattered results during cycles 1-15 were due to the effect of varying such conditions in an effort to increase throughput. Cycles 16-25 and 26-35 consisted of two series of 10 subsequent cycles each for \( P_{\text{solar}} = 3.8 \) kW and optimized conditions as presented in Figure 2.5. A strong decrease in temperature and, consequently, in CO rate was observed with cycle number. This decrease was attributed to sublimation of ceria and its condensation on the refrigerated CPC, lowering the radiative power input to the cavity as previously observed. As expected, the values of temperature and CO rate resumed to the initial values after cleaning the CPC between cycles 25 and 26. This phenomenon was less pronounced in cycles 36-45 because of lower radiative power (\( P_{\text{solar}} = 2.8 \) kW), which led to lower temperatures (below 1450 °C) and lower but stable CO rates from cycle to cycle.
Figure 2.6. Nominal solar reactor temperature at the end of the reduction step and peak CO and \(\text{H}_2\) production rates versus cycle number for 291 redox cycles, measured with the solar reactor containing DS-RPC. Region I (cycles #1-45; close-up in Figure 2.7): \(\text{CO}_2\) splitting cycles under varying experimental conditions of \(P_{\text{solar}} = 2.8\text{-}3.8\) kW during reduction, \(P_{\text{solar}} = 0\) kW during oxidation, and \(V_{\text{Ar}} / V_{\text{CO}_2} = 2\text{-}10\) L min\(^{-1}\). Region II (cycles #46-60): \(\text{H}_2\text{O}/\text{CO}_2\)-splitting cycles at \(P_{\text{solar}} = 3.8\) kW during reduction, \(P_{\text{solar}} = 0\) kW during oxidation, and various flow configurations. Region III (cycles # 61-227): 166 consecutive \(\text{H}_2\text{O}/\text{CO}_2\)-splitting cycles at \(P_{\text{solar}} = 3.8\) kW and \(V_{\text{Ar}} = 8\) L min\(^{-1}\) for 20 min during reduction, 8 min cooling, and \(P_{\text{solar}} = 0\text{-}0.8\) kW at 750 °C with \(V_{\text{CO}_2} = 0.5\) L min\(^{-1}\) + \(V_{\text{H}_2\text{O}} = 2.4\) L min\(^{-1}\) for 8 min during oxidation. Region IV (cycles #227-291): 64 consecutive \(\text{H}_2\text{O}/\text{CO}_2\)-splitting cycles at similar operating conditions as in Region III but with fresh RPCs.
Figure 2.7. Nominal solar reactor temperature at the end of the reduction step and peak CO and H$_2$ production rates versus cycle number of CO$_2$ splitting cycles under varying experimental conditions of $P_{\text{solar}} = 2.8$-$3.8$ kW during reduction, $P_{\text{solar}} = 0$ kW during oxidation, and $\dot{V}_{\text{Ar}} / \dot{V}_{\text{CO2}} = 2$-$10$ L min$^{-1}$ (close-up of Region (I) in Figure 2.6).

Figure 2.8. Nominal reactor temperature and O$_2$, CO and H$_2$ evolution rates of representative cycles #216-217 from region III in Figure 2.6.
Region II (cycles #46-60) in Figure 2.6 presents the co-production of H₂ and CO by simultaneously splitting a mixture of H₂O and CO₂, performed at varying flow and H₂O:CO₂ ratios to find appropriate baseline conditions for cyclic operation. The radiative power input during the reduction step was kept constant for these cycles at \( P_{\text{solar}} = 3.8 \text{ kW} \). Various inert gas flow configurations were explored to avoid ceria condensation on the CPC, indicating that injecting inert gas radially at the plane close to the quartz window resulted in the best aerodynamic protection. The co-feeding molar ratio H₂O:CO₂ was varied to examine its influence on the H₂:CO molar ratio in the product gas stream. In agreement with previous results, increasing the H₂O:CO₂ ratio yielded syngas with a higher H₂:CO molar ratio. Lowering the total reactant gas flow rate resulted in an increase of the syngas concentration, i.e., higher conversion of H₂O and CO₂ because of longer residence time, but at the expense of lower syngas throughput. Co-feeding a mixture of H₂O and CO₂ at a molar ratio of 4.8 and a total flow rate of 2.9 L min\(^{-1}\) for 7-10 min resulted in syngas with a H₂:CO molar ratio of roughly 1.7 and a total syngas concentration above 50% in the product gas stream. Figure 2.8 shows the nominal solar reactor temperature and O₂, CO, and H₂ concentrations for two representative cycles (# 216-217) performed under these conditions.

Region III (cycles # 61-227) in Figure 2.6 shows 166 consecutive H₂O/CO₂-splitting cycles where the reactor temperature was stabilized during oxidation at around 750 °C with \( P_{\text{solar}} = 0.8 \text{ kW} \) and the oxidation was terminated when the syngas concentration dropped below 40%. Also indicated are linear fits of the nominal reactor temperature and H₂/CO production rates, which slightly decreased with cycle number. We attributed the decreasing temperature and rates mainly to sintering of the insulation which shifted the RPC rings out of center, causing blocking and non-uniform absorption of incoming concentrated radiation. In addition, a slight decrease in SSA due to grain growth (cf. Figure 2.9, discussed later) may have affected the peak rates.
Region IV (cycles # 227-291) in Figure 2.6 shows 64 consecutive cycles performed under similar operating conditions as in Region III but with fresh RPCs. Here we observed increasing reactor temperatures and H$_2$ rates with cycle number. The former is attributed to an increase of the time duration of the reduction step in an effort to maximize $\delta$ and total syngas throughput (rather than $\eta_{\text{solar-to-fuel}}$). The latter is attributed to an increasing H$_2$O:CO$_2$ co-feeding ratio to obtain higher H$_2$:CO ratio in the collected syngas. The total syngas production rate increased from cycle to cycle which indicated the strong effect of the solar reactor temperature during thermal reduction on the fuel output per cycle.

Figure 2.9 shows SEMs of a strut surface (top row) and cross section (bottom row) for: (a) the unreacted RPC sample; (b) after 227 cycles collected from the outer perimeter of a ring (facing towards insulation, minimum radiation flux); and (c) after 227 cycles collected from the directly irradiated inner perimeter (maximum radiation flux). After 227 cycles, the RPC was exposed to a total of 127 h of concentrated radiation. The integrity of the porous struts was maintained throughout cycling, irrespective of the position within the reactor. A more pronounced grain growth was observed for the directly irradiated sample because of the higher temperatures at this location, but the interconnected porous network was not lost. Preservation of the open porosity was confirmed by mercury intrusion porosimetry measurements, which indicated open strut porosity before and after 227 cycles of 24% and 23%, respectively. The mean pore diameter increased from 1.8 to 6.4 µm and the specific surface area decreased from 0.109 to 0.029 m$^2$ g$^{-1}$ (based on the assumption of cylindrical pores). It should be noted that these values are not consistent with the SEM analysis, presumably due to the presence of ink-bottle pores (pores with a narrow throat) that can falsify the pore diameter observed by mercury porosimetry.\textsuperscript{100-101}

Overall, the RPC exhibited superior stability over multiple cycling under solar concentrating conditions. Previously synthesized high
SSA structures with sub-micron sized features showed high oxidation rates, but underwent extensive sintering at the required reduction temperatures.\textsuperscript{102-104} In contrast to these structures with sub-micron sized features, our DS-RPC uses larger pores that offer a slightly lower initial surface area, but in return the morphology is more stable at the required reduction temperatures. Additionally, the large scale pores in the mm-range avoid overheating of the irradiated surface by volumetric absorption, further diminishing sintering problems at these critical locations.

**Figure 2.9.** SEM micrographs of strut surfaces (top) and break planes (bottom) of samples: (a) freshly produced RPC; (b) outer perimeter of an RPC ring after 227 cycles; and (c) directly irradiated inner perimeter of an RPC ring after 227 cycles.
2.2.2 Liquid Fuel Synthesis

The syngas produced during 243 cycles (regions III and IV of Figure 2.6) was collected and compressed into a 5 L standard aluminum gas bottle to a final pressure of 150 bar at room temperature. This corresponded to 700 standard liters of syngas with a final composition of 33.7 % H₂, 19.2 % CO, 30.5 % CO₂, 0.06 % O₂, 0.09 % CH₄, and 16.5 % Ar. Unreacted H₂O was condensed and separated. Adverse poisons for FT-catalysts were not detected at a lower detection limit (LOD) of 1 ppb by PTR-MS. The trace amount of O₂ was presumably due to O₂ still trapped in the pipes when switching from reduction to oxidation mode, while CH₄ was likely formed by methanation on catalytic metallic surfaces. The H₂:CO molar ratio was 1.76, which fits the targeted syngas quality for FT-synthesis, proving the good controllability of the process. Traces of Ni(CO)₄ were detected downstream of the compressor station (but not at the exit of the solar reactor), indicating its formation by CO reacting with stainless steel piping at high pressures. Its formation can be avoided by using Ni-free components in the compression and storage unit.

The $\eta_{\text{solarto-fuel}}$ averaged over the 243 consecutive cycles was 0.77 %. Note that during these cycles heat recovery was not implemented and the operating conditions were not optimized for efficiency (as described in Figure 2.5) but for syngas yield, as the aim – besides stability evaluation – was to collect 700 L of syngas during minimum experimental time. As for the high content of unreacted CO₂ in the syngas (30.5%), it was found that its presence does not affect the FT-processing. The energy wasted in heating the unreacted CO₂ was accounted for in the calculation of $\eta_{\text{solarto-fuel}}$, Equation 2.1, and represented only 0.026 % of the solar power input $P_{\text{solar}}$. However, if CO₂ recovery is desired, its separation from syngas would cause an additional energy penalty of at least (theoretically) 1.5 kJ mole⁻¹ of syngas, corresponding to approximately 1 % of the syngas’s high heating value.
85% of the collected syngas was subsequently processed in a small-scale FT reactor using Co-based catalysts at Shell Global Solutions, Amsterdam, yielding 40.6 g of liquid products and 48.1 g of solid waxes. A small fraction of the produced wax (7.2%, 3.46 g) was hydrocracked in a batch-type reactor and yielded 2.79 g of liquid hydrocarbons with the following composition: 17.1 wt% naphtha (boiling range 0-145 °C), 35.6 wt% kerosene (145-300 °C), 17.1 wt% gasoil (300-370 °C), and 30.2 wt% of heavier fractions (>370 °C). This is the first ever production of jet fuel by solar thermochemical splitting of CO$_2$ and H$_2$O. No attempt was undertaken to optimize the gas-to-liquid process. The selectivity to kerosene can be made to exceed 50%.

The results of this experimental campaign demonstrated the technical feasibility of the solar redox process at operating conditions relevant to industrial scale implementation. The RPC is the most critical component of the solar reactor and its deterioration can occur because of crack formation, side reactions, sintering, and/or sublimation. Cracks result from stresses induced by thermal and chemical expansion during the temperature swing between redox steps. Smaller temperature gradients and avoiding thermal shocks (by slower heating/cooling rates) can alleviate the formation of cracks but at the expense of a less optimal operational mode in terms of energy efficiency. Side reactions result through contact of ceria with other materials (e.g. insulation), and can be eliminated by adding an inner insulation layer made of pure CeO$_2$ as applied in this study. Sintering detrimentally affects the oxidation rate because of decreasing reactive surface area, and it can be diminished by the appropriate choice of the pore size, as discussed in previous sections. Finally, sublimation of the active material at overheated spots leads to a loss of active material and upon condensation it can affect the functionality of system components such as the transparent quartz window and the reflective secondary concentrator. Appropriate flow configurations can help protect these components, while the geometrical design of the cavity
can support uniform radiative heat transfer and temperature
distribution to avoid overheated spots.

2.2.3 Comparison to Other Renewable Liquid Fuel Production
Routes

Energy conversion efficiencies of growing biomass and processing it
to liquid biofuels are typically below 1% as a result of the inherent
energy irreversibilities of photosynthesis.\textsuperscript{9-10} Thus, growth of energy
crops on all unused cultivable land on earth would cover less than 10
TW and would not meet the scale of future global demand.\textsuperscript{1}
Photocatalytic water-splitting technology suffers from even lower
efficiencies of the order of 0.1 \%,\textsuperscript{11-12} and thus would require an
increase by at least 2 orders of magnitude to render an economically
feasible approach.\textsuperscript{108} On the other hand, solar-to-H\textsubscript{2} energy conversion
efficiencies around 12\% can be accomplished by water electrolysis
driven with PV electricity\textsuperscript{13-14} and by photo-electrochemical cells,\textsuperscript{15-17}
but several additional steps and associated energy penalties should be
accounted for the conversion of H\textsubscript{2} to liquid hydrocarbons if liquid
fuels are targeted. An overall efficiency of 8.2\% is estimated assuming
intermediate efficiencies of 19\% for PV, 85\% for water electrolysis,
80\% for voltage mismatch, 90\% for reverse water-gas shift (RWGS),
and 70\% for Fischer-Tropsch synthesis.\textsuperscript{109} Not included in this
estimation is the need for energy/fuel storage due to the intermittency
of solar radiation, which introduces additional energy and cost
penalties. Comparable efficiencies are achieved using concentrated
solar thermal electricity, also known as CSP, with the additional
advantage of round-the-clock operation when integrated with a
thermal storage unit.\textsuperscript{110} Synthesis of CO from CO\textsubscript{2} using a photo-
electrochemical cell was recently demonstrated at an efficiency of
6.5\%.\textsuperscript{18}

The solar thermochemical fuel path uses the same solar concentration
infrastructure as CSP to collect the entire solar spectrum and deliver
high-temperature heat directly to the endothermic solar reactor,
bypassing the two energy conversion stages of electricity production
and electrolysis, and thus has the potential of exceeding the aforementioned efficiencies. The capability of the solar reactor to capture the concentrated solar energy is characterized by its absorption efficiency $\eta_{\text{absorption}}$, defined as the net rate at which heat is being absorbed divided by the solar power coming from the solar concentrator. For a perfectly insulated blackbody cavity-receiver, it is given by

$$\eta_{\text{absorption}} = 1 - \left( \frac{\sigma T^4}{IC} \right)$$  \hspace{1cm} (2.3)

$T$ is the nominal cavity-receiver temperature, and $\sigma$ the Stefan-Boltzmann constant. Values of the solar flux concentration ratio $C$ are typically obtained at the level of 1000 suns for centralized (MW) solar tower systems and 10,000 suns for decentralized (kW) dish systems. To some extent, the flux concentration can be further augmented with the help of a CPC and other secondary concentrators positioned in tandem with the primary parabolic concentrator, as implemented in the solar reactor’s aperture in this study. Higher $C$ imply lower heat losses from smaller areas and, consequently, higher $\eta_{\text{absorption}}$.

Overall energy conversion efficiencies of solar-driven photochemical, electrochemical, thermochemical processes and their combinations have a direct impact on the economics of the process, as the major cost component derives from the investment of the large-area solar collection infrastructure. A detailed techno-economic analysis for the complete process chain of the solar thermochemical production of methanol from $\text{H}_2\text{O}$ and $\text{CO}_2$, similar to the pathway used in this study, indicated a cost of 1.22 USD per kg methanol, which while higher than current market prices is comparable to other renewable based fuel alternatives.\footnote{This cost estimate was obtained assuming $\eta_{\text{solar-to-fuel}} = 20\%$ for $\text{CO}_2$-splitting, the water-gas-shift (WGS) for the generation of syngas, and an overall solar-to-MeOH energy conversion efficiency of 7.1\% based on the high heating value of MeOH at 726 MJ/kmol. A follow-up system-level study that also considered CO$_2$ flue-gas}
capture and transport indicated a methanol cost in the range 4.24 – 6.73 USD per gallon gasoline equivalent.\textsuperscript{112} Solar syngas is either obtained by splitting CO\textsubscript{2} with subsequent WGS, splitting of H\textsubscript{2}O with subsequent RWGS, or by co-splitting both H\textsubscript{2}O and CO\textsubscript{2} to directly produce syngas of desired stoichiometry as shown experimentally in this study. Interestingly, the latter approach of co-splitting CO\textsubscript{2} and H\textsubscript{2}O in the solar reactor is favored because it bypasses the inefficiencies and energy penalties arising from the WGS/RWGS reactors, leading to an overall solar-to-MeOH energy conversion efficiency of 11.7%. If syngas is processed to Fischer-Tropsch products instead, the overall efficiency is comparable at 11.3%, while the cost is slightly penalized because of the lower yield but compensated by the higher market value of FT-products compared to methanol.\textsuperscript{112} Furthermore, in contrast to biofuels,\textsuperscript{10} a life cycle analysis indicates that the solar-driven thermochemical approach offers significant advantages in terms of global warming potential of discharged greenhouse gases.
2.3 Summary and Conclusions

A reticulated porous ceramic (RPC) structure made from pure CeO$_2$ with porosities on two different length scales ($d_{\text{mean}} = 2.5$ mm and 10 µm), was characterized in a solar cavity-type reactor during 291 thermochemical redox cycles for splitting CO$_2$ and H$_2$O. The large scale pores enabled volumetric absorption of incoming radiation whereas the smaller pores in the struts increased the specific surface area, enhancing the surface-limited fuel production rates. For $P_{\text{Solar}} = 3.8$ kW, the optimized cycle duration was 25 min (8 min reduction, 2 min cool-down, and 15 min oxidation), yielding a $\eta_{\text{solar-to-fuel}}$ of 1.72%. Chemical yields and rates were largely stable over the course of 227 consecutive cycles. SEM images revealed grain growth and moderate sintering, but no loss in open porosity was detected. Compared to the SS-RPC (no strut porosity), the DS-RPC exhibited higher fuel rates and throughput per mass of active material.

Finally, to the best of our knowledge, this was the first experimental coupling of solar syngas production from H$_2$O and CO$_2$ with the compression, storage, and FT-processing to liquid hydrocarbons. FT-processed kerosene, derived from H$_2$O and CO$_2$, can be certified for commercial aviation by minor addendum to the existing D7566 specification for synthesized hydrocarbons.
Chapter 3

Design and Testing of an Optimized Solar Reactor‡

In this chapter, the design optimization and experimental testing of a 4 kW solar reactor for splitting of H₂O and CO₂ via ceria redox reactions is presented. The solar reactor consists of a windowed cavity-receiver containing a reticulated porous ceramic (RPC) foam-type structure made of ceria, which is directly exposed to concentrated solar radiation. Monte-Carlo ray tracing and CFD simulations were applied to determine the optimal geometry to reach uniformity of the radiative flux over the RPC surface and fluid flow across the RPC. Experimentation was carried out with varying radiative power input (2.4-4.1 kW), reduction temperature (1450-1550 °C), purge Ar gas flow rate during reduction (4-13 L min⁻¹), oxidation temperature (750-1200 °C), and H₂O/CO₂ flow rate during oxidation (1-7 L min⁻¹).

‡ Material in this chapter will be submitted for publication as: D. Marxer, P. Furler, F. Pfleiderer, F. Caduff, P. Haueter and A. Steinfeld, “Optimized solar reactor with a ceria foam structure for redox splitting of H₂O and CO₂.”
3.1 Motivation

In parallel to the experimental studies (Chapter 2), a 3D heat and mass transfer model of the gen-1 reactor prototype revealed optimization potential in terms of geometrical design and flow configuration. It was observed that the temperature distribution inside the cavity strongly depended on the distribution of the incoming radiative flux and reached critical values at highly exposed regions where ceria underwent sublimation or local melting of the Al₂O₃-SiO₂ insulation occurred. Further complications arise from a buoyancy-driven natural convection flow, created by large temperature gradients between the hot cavity and the actively-cooled reactor front, carrying CeO₂(g) towards the front where it eventually condensed on the CPC’s surface and quartz window, thereby reducing its reflectivity and transmissivity, respectively, and consequently attenuating the radiative power input through the aperture. In this chapter, the design, fabrication and experimental characterization of an optimized solar reactor (gen-2) is presented that avoids the aforementioned problems, which features superior geometry for uniform temperature distribution and a controlled flow field across the RPC for preventing backflow of gases towards the quartz window, ultimately leading to a higher solar-to-fuel energy conversion efficiency.

3.2 Solar Reactor Design and Experimental Setup

Figure 3.1 (a) shows a schematic of the optimized solar reactor (gen-2). It consists of a windowed cavity-receiver containing a reticulated porous ceramic (RPC) structure made of pure ceria. The cavity has a 4 cm-diameter aperture, an inner diameter of 100 mm and depth of 75 mm, with an RPC thickness of 25 mm lined by fibrous CeO₂ and Al₂O₃-SiO₂ insulation layers. The reactor front is sealed by an 11 cm-diameter, 4 mm-thick clear fused quartz disk window. Figure 3.1 (b) and (c) show photographs of the solar reactor setup and the solar reactor during operation in the HFSS, respectively.
Figure 3.1. (a) Schematic of gen-2 solar reactor. It consists of a windowed cavity-receiver containing a reticulated porous ceramic (RPC) foam-type structure, made of ceria, which is directly exposed to concentrated solar radiation entering through the cavity’s aperture. Red arrows indicate inlet and outlet flows. (b) Photograph of the solar reactor setup. (c) Photograph of the solar reactor during operation in the HFSS.
Modelling – Monte-Carlo (MC) ray-tracing simulations and a previously developed and validated 3D heat transfer and fluid flow model were applied to improve the cavity geometry and the flow field. Figure 3.2 shows a schematic of the computational domains and the applied boundary conditions used for the CFD simulations. To find a suitable flow configuration at minimum computational cost, steady-state simulations with fixed RPC and window temperatures were conducted. The fluid domains (reactor front, cavity, gas gap and outlet) were assumed to be non-participating and laminar flow conditions were assumed in all domains. The insulation layers (ceria and Al₂O₃-SiO₂) were modelled as solid domains whereas the ceria RPC was modeled as an isotropically participating, two-phase porous domain. The governing equations in the fluid domains are given by: \(^{113}\)

Continuity:
\[
\nabla \cdot (\rho \overline{U}) = 0 \tag{3.1}
\]

Momentum conservation:
\[
\nabla \cdot \left( \rho \overline{U} \overline{U} \right) = -\nabla p + \nabla \cdot \mu \left( \nabla \overline{U} + \left( \nabla \overline{U} \right)^{T} - \frac{2}{3} \overline{I} \cdot \nabla \right) + \overline{S}_{M,buoy} \tag{3.2}
\]

Energy conservation:
\[
\nabla \cdot \left( \overline{U} \rho h \right) = \nabla \cdot (k \nabla T) \tag{3.3}
\]

where \( \rho \) denotes the density, \( \overline{U} \) the velocity, \( h \) the enthalpy, \( \overline{I} \) the identity matrix, \( \mu \) the dynamic viscosity, \( \overline{S}_{M,buoy} \) the momentum source to account for buoyancy, and \( k \) the thermal conductivity of Ar.

In the solid domains the energy conservation equation is given by:
In the fluid phase of the porous RPC, the governing equations are:

Continuity:

\[
0 = \nabla \cdot (k \nabla T) \quad (3.4)
\]

Momentum conservation:

\[
\nabla \cdot \left( \rho \bar{K} \cdot \bar{U} \right) = 0 \quad (3.5)
\]

\[
\nabla \cdot \left( \rho \bar{K} \cdot \bar{U} \right) = -\nabla p + \left( \nabla U + \left( \nabla U \right)^T - \frac{2}{3} \nabla \cdot \nabla \right) + S_{M,buoy} + S_{M,porous} \quad (3.6)
\]

Energy conservation:

\[
\nabla \cdot \left( \rho \bar{K} \cdot \bar{U} \right) = \nabla \cdot (k \nabla T) + Q_{fs} \quad (3.7)
\]

where \( \varepsilon \) is the volume porosity, \( S_{M,porous} \) the momentum source to account for the viscous loss and inertial drag force from the porous structure according to the Dupuit-Forchheimer law, and \( \bar{K} \) is the isotropic porosity tensor. Energy exchange between the fluid and solid in the porous RPC domain is given by the source term \( Q_{fs} \), defined as:

\[
Q_{fs} = h_{fs} \cdot A_{fs} \cdot (T_s - T_f) \quad (3.8)
\]

where \( A_{fs} \) is the fluid-solid area density, \( T_s \) is the solid (ceria) temperature, \( T_f \) is the gas temperature, and \( h_{fs} \) is the heat transfer coefficient between the RPC and the gas phase, calculated from direct pore-level numerical simulations on the exact RPC geometry obtained by 3D tomographic scans.\(^{98}\)

The same material properties as in a previous study\(^{113}\) were used and are listed in Table 3.1. The heat capacities of the insulation materials were determined by differential scanning calorimetry.\(^{113}\) The thermal
cond conductivity of the ceria insulation was measured by laser flash analysis.\cite{113} The thermal conductivity of the Al$_2$O$_3$-SiO$_2$ insulation was taken from manufacturer data.\cite{114} The mass transfer properties of the porous domain were determined from pore-level simulations.\cite{97-98,115}

The boundary conditions are indicated in Figure 3.2. The water cooled surfaces were assumed to be at 300 K. The window was modelled as a wall at $T = 700$ K. Ar was injected to the gas inlet nozzles at 300 K. The solid in the porous RPC domain was modelled isothermal at $T = 1773$ K to approximate the situation at the end of the reduction step and to save computational cost. Radiation was not included. Natural convection was assumed at the outer reactor surface and was modelled using Nusselt correlations for a vertical flat plate and a horizontal cylinder.\cite{116-117}

Simulations were performed with the CFD code ANSYS CFX 15.0. The governing equations were discretized in space (3.3 million tetrahedrons) and solved on the individual control volumes by the finite-volume method with a first order upwind scheme.

The radiative flux distribution inside the cavity was calculated using 3D MC ray-tracing simulations of the high flux solar simulator with the reactor in the focal position. The cavity geometry and dimensions were varied to yield a uniform flux distribution. The single lamps of the HFSS were modeled as spherical radiation sources, surrounded by two electrodes, a quartz bulb, and truncated ellipsoidal reflectors (specular reflectivity = 0.85, reflection error angle = 3.5 mrad). The optical properties of the polished alumina surfaces (specular, surface emittance $\varepsilon_s = 0.1$), and of the Al$_2$O$_3$-SiO$_2$ insulation (diffuse, $\varepsilon_s = 0.28$) were taken from literature.\cite{118-120} The RPC surface was modeled as blackbody absorber for determining the incident flux distribution. The quartz window was modeled as thin layer with a total surface reflectance and a transmittance of 0.06 and 0.94, respectively. The MC simulations were performed using the in-house code VEGAS\cite{121} with $3.5 \cdot 10^8$ rays.
Table 3.1. Material properties used for CFD and MC simulations. Table adapted from reference.\textsuperscript{113}

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CeO$_2$ RPC</strong></td>
<td>Density (kg m$^{-3}$)</td>
<td>7220</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Porosity (%)</td>
<td>63</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Permeability ($\text{m}^2$)</td>
<td>4.63376$\times$10$^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dupuit-Forchheimer coefficient ($\text{m}^{-1}$)</td>
<td>1616.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity solid (W m$^{-1}$ K$^{-1}$)</td>
<td>($17.8004$-$0.02402\cdot T$+$0.0000112032\cdot T^2$-$1.7\cdot10^{-9}\cdot T^3$)</td>
<td>280 – 2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($9.79799$+$0.00483384\cdot T$-$3.3397\cdot10^{-6}\cdot T^2$+$2.8\cdot10^{-9}\cdot T^3$)</td>
<td>&gt; 2000</td>
</tr>
<tr>
<td></td>
<td>Specific heat capacity (J kg$^{-1}$ K$^{-1}$)</td>
<td>$-0.0001271\cdot T^2$+$0.2697656\cdot T$+$299.8695684$</td>
<td>280 – 1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($444.27$)</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td></td>
<td>Fluid-solid Nusselt number (-)</td>
<td>$e_0$+$e_1\cdot T$+$e_2\cdot T^2$+$e_3\cdot T^3$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fluid-solid area density ($\text{m}^{-1}$)</td>
<td>952</td>
<td>-</td>
</tr>
<tr>
<td><strong>Al$_2$O$_3$-SiO$_2$ Insulation</strong></td>
<td>Density (kg m$^{-3}$)</td>
<td>560.65</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Specific heat capacity (J kg$^{-1}$ K$^{-1}$)</td>
<td>$4\cdot10^{-7}\cdot T^2$+$1.5987289\cdot T$+$477.6995948$</td>
<td>$\leq 1480$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($1118.44$)</td>
<td>$\geq 1480$</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity (W m$^{-1}$ K$^{-1}$)</td>
<td>$0.00012926\cdot T^2$+$0.019654$</td>
<td>280-2200</td>
</tr>
<tr>
<td></td>
<td>Hemispherical total emittance</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td><strong>CeO$_2$ Laminate</strong></td>
<td>Density (kg m$^{-3}$)</td>
<td>504.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Specific heat capacity (J kg$^{-1}$ K$^{-1}$)</td>
<td>$-0.0001271\cdot T^2$+$0.2697656\cdot T$+$299.8695684$</td>
<td>280 – 1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($444.27$)</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity (W m$^{-1}$ K$^{-1}$)</td>
<td>$2.2\cdot10^{-7}\cdot T^2$+$2.8387\cdot10^{-4}\cdot T$+$0.17678688$</td>
<td>295 - 2000</td>
</tr>
<tr>
<td><strong>Argon</strong></td>
<td>Thermal conductivity (W m$^{-1}$ K$^{-1}$)</td>
<td>$2.35332617\cdot10^{-12}\cdot T^2$+$1.289997670118\cdot10^{-8}\cdot T^2$+$4.83706137185442\cdot10^{-9}\cdot T^2$+$0.00483418574527758$</td>
<td>290 - 2400</td>
</tr>
<tr>
<td></td>
<td>Dynamic viscosity (kg m$^{-1}$ s$^{-1}$)</td>
<td>$3.51928\cdot10^{-15}\cdot T^2$+$2.045615632\cdot10^{-11}\cdot T^2$+$6.84961187335571\cdot10^{-8}\cdot T$+$4.20667800364964\cdot10^{-6}$</td>
<td>290 - 2400</td>
</tr>
</tbody>
</table>
Figure 3.2. Schematic of the fluid, solid and porous domains and the boundary conditions used for CFD simulations.

Figure 3.3 shows the computed radiative flux distribution impinging on the exposed Al₂O₃-SiO₂ insulation and RPC surface inside the cavity at $P_{solar} = 3.8$ kW for: (a) the previously tested gen-1 solar reactor (Chapter 2); and (b) the optimized gen-2 solar reactor. The gen-1 exhibited a strongly non-uniform flux distribution with a peak flux $> 8 \cdot 10^5$ W m⁻², partly because of the compound parabolic concentrator (CPC) which directs the incoming radiation mostly onto areas close to the aperture. In the gen-2 design the secondary concentrator was omitted and the cavity diameter was increased to ensure that the radiative power is distributed over the cavity depth while still keeping a high apparent absorptivity (0.987). The peak flux observed for the gen-2 design was $2.5 \cdot 10^5$ W m⁻² and resulted from the individual Xe-arcs of the HFSS.
Figure 3.3. Incident radiative heat flux distribution in the inner walls of the solar reactor’s cavity at $P_{\text{solar}} = 3.8$ kW for:

(a) the gen-1 solar reactor; and (b) the gen-2 solar reactor.
Figure 3.4 shows the normalized velocity vectors and the velocity contour plot for two flow configurations: (a) $\dot{V}_{Ar} = 4 \text{ L min}^{-1}$ equally distributed among 6 radial gas inlet nozzles close to the quartz window; and (b) $\dot{V}_{Ar} = 3 \text{ L min}^{-1}$ equally distributed among 6 tangentially tilted nozzles close to the quartz window and $\dot{V}_{Ar} = 1 \text{ L min}^{-1}$ equally distributed among 4 additional vertical nozzles behind the aperture. Configuration (a) is undesired because of the buoyancy-driven natural convection which carries CeO$_2$(g) to the reactor front, as previously described. This back-flow can be effectively eliminated with configuration (b) by tilting the inlet nozzles by 30° relative to the radial direction and by placing additional inlet nozzles behind the aperture. This arrangement extinguishes the buoyancy-driven flow and creates a stable aerodynamic curtain that protects the window from condensables. Additionally, multiple outlet ports and gaps create a uniform flow across the RPC.
Figure 3.4. Normalized velocity vectors and contours in the vertical cross-section of the solar reactor for: (a) $\dot{V}_{\text{Ar}} = 4 \text{ L min}^{-1}$ equally distributed among 6 radial inlet nozzles close to the window; and (b) $\dot{V}_{\text{Ar}} = 3 \text{ L min}^{-1}$ equally distributed among 6 tangential inlet nozzles close to the window and $\dot{V}_{\text{Ar}} = 1 \text{ L min}^{-1}$ equally distributed among 4 nozzles behind the aperture.
Experimental Setup – Experimentation was performed at ETH’s high-flux solar simulator (HFSS) which was described in Section 2.1. The radiative flux distribution at the focal plane was measured optically using a calibrated CCD camera focused on a Lambertian (diffusely reflecting) target. $P_{\text{solar}}$ was measured by a water calorimeter. Temperatures were measured at the outer surface of the RPC with B-type thermocouples. Reacting gases were injected through 6 tangential inlet ports behind the window and 4 inlet ports behind the aperture, and product gases exited through 5 outlet ports at the rear plate. Ar (99.996% purity) and CO$_2$ (99.998% purity) flow rates were regulated by electronic mass flow controllers (Bronkhorst F-201 C). Demineralized H$_2$O was delivered at 150 °C by a steam generator (Bronkhorst W-202A-333K) that was regulated by a liquid mass flow controller (Bronkhorst L2-FAC-11-0). Product gas composition was monitored by gas chromatography (Varian 490), supplemented by an electrochemical sensor for O$_2$ (Siemens Ultramat 23), infrared-based detectors for CO and CO$_2$ (Siemens Ultramat 23), and a thermal conductivity based detector for H$_2$ (Siemens Calomat 6).

The nonstoichiometry distribution of the CeO$_2$ RPC inside the reactor was determined by cooling the reactor to room-temperature after thermal reduction under an Ar-flow to avoid re-oxidation. The RPC was then extracted, segmented into samples for spatial discretization, and the samples where weighed. After re-oxidation in air at 300 °C for 10 h, the samples where weighed again and the nonstoichiometry was calculated from the mass increase.

RPC fabrication – The ceria RPC parts were fabricated by the replication method with a subsequent infiltration step.$^{92-93}$ Cerium(IV)-oxide powder (particle size <5 µm, 99.9 % purity, Sigma-Aldrich) was mixed with 15 wt% water, 30 vol% of spherical carbon pore-forming agent particles (particle size 0.4-12 µm, HTW Hochtemperatur-Werkstoffe GmbH), 0.83 wt-% organic deflocculating agent (Dolapix CE 64), polyvinyl alcohol binder (Optapix RA 4G), and antifoaming agent (Contraspum KWE), and
processed according to a previously published recipe. Organic polyurethane sponges of 10 ppi (Foam-Partner, Fritz Nauer AG) were then immersed into the slurry, dried in air, and sintered in an electrical furnace at 1600 °C. Figure 3.5 (a) shows SEM micrographs (Hitachi TM-1000) of the cross section of the dual-scale RPC with pores in the millimeter and micrometer ranges. The triangular void space in the center of the struts resulted from the replication method. In this work, we filled the hollow struts with a porous ceria matrix by a vacuum-ultrasonic infiltration technique to improve its mechanical stability. Infiltration was performed by immersing the sintered foams into a low-viscosity slurry under vacuum pressure (50 mbar). The pressure was then increased to 1 bar and the immersed RPC was excited in an ultrasonic bath. Finally, the foams were removed from the slurry, dried, and sintered at 1600 °C. Figure 3.5 (b) shows a strut cross section of an infiltrated dual-scale RPC as used in this work. Figure 3.5 (c) and (d) show photographs of the ceria RPC parts and of the assembled solar reactor’s cavity, respectively. Bricks of RPC were arranged in an octagonal shape inside the cavity to avoid cracking by allowing for thermal and chemical expansion of the structure. The total CeO₂ RPC mass load was 1728 g.
Figure 3.5. (a) SEM micrograph of strut cross-section of the dual-scale RPC with hollow strut (without infiltration) as used in previous studies. \(^{68, 125}\) (b) Strut cross-section of the dual-scale RPC with infiltrated strut as used in this study. (c) Photograph of ceria RPC bricks. (d) Assembled RPC bricks in an octagonal shape inside the solar reactor’s cavity.
3.3 Experimental Results and Discussion

During a typical redox cycle, the solar reactor was first heated by \( P_{\text{solar}} = 2.4 \text{ – } 4.1 \text{ kW} \) to the desired reduction temperature in the range \( T_{\text{reduction}} = 1450\text{-}1550 \text{ °C} \) while purging with Ar flow rates \( \dot{V}_{\text{Ar}} \) ranging from 4 to 13 L min\(^{-1} \). Following reduction, the HFSS was turned off \( (P_{\text{solar}} = 0) \) and the reactor was cooled to the desired oxidation temperature in the range \( T_{\text{start oxidation}} = 750\text{-}1200 \text{ °C} \). Subsequently, oxidation was performed by injecting the reactant gas, either \( \text{CO}_2 \) or a mixture of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). Once oxidation was completed at \( T_{\text{end oxidation}} \), the next cycle was initiated. Since during the oxidation step \( P_{\text{solar}} = 0 \), in the following we will refer to \( P_{\text{solar}} \) to the solar radiative power input during the reduction step only.

Unless noted, all experimental results in this chapter are presented for the gen-2 solar reactor. Its performance is characterized by the solar-to-fuel energy conversion efficiency \( \eta_{\text{solar-to-fuel}} \), defined as:

\[
\eta_{\text{solar-to-fuel}} = \frac{\Delta H_{\text{fuel}} \int r_{\text{fuel}} dt}{\int P_{\text{solar}} dt + \frac{1}{\eta_{\text{heat-to-work}}} E_{\text{inert}} \int r_{\text{inert}} dt} \tag{3.9}
\]

where \( \Delta H_{\text{fuel}} \) is the heating value of the fuel produced, \( r_{\text{fuel}} \) is the molar rate of fuel produced, \( P_{\text{solar}} \) is the radiative power input through the reactor’s aperture (corrected for the quartz window transmittance, assumed 93.2 %)\(^{126,127} \), \( r_{\text{inert}} \) is the inert gas flow rate during reduction, \( E_{\text{inert}} \) is the work required for inert gas separation (assumed 20 kJ per mole of Ar)\(^{96} \) and \( \eta_{\text{heat-to-work}} \) is the heat-to-work conversion efficiency (assumed 0.4)\(^{4,53,128} \). Note that in previous studies \( \eta_{\text{heat-to-work}} \) and the losses at the quartz window were not included.\(^{51,67,71,113,125} \)

**Argon flow rate** – The use of Ar purge gas during the reduction step (Equation 1.5) to lower the \( p_{\text{O}_2} \) introduces an energy penalty to the process because of the need to separate Ar from Ar/\( \text{O}_2 \) mixtures.\(^{53,128} \) We therefore assessed the influence of the flow rate of Ar, \( \dot{V}_{\text{Ar}} \), on the process performance experimentally. Figure 3.6 (a) shows the
nominal solar reactor temperature and the specific\textsuperscript{§} O\textsubscript{2} and CO evolution rates during five CO\textsubscript{2}-splitting redox cycles, each at different Ar flow rate during the reduction step: 4, 7, 10, and 13 L min\textsuperscript{-1}. In these experimental runs, the reactor was heated with $P_{\text{solar}} = 2.9$ kW to 1450 °C while $\dot{V}_{\text{Ar}} = 4$-13 L min\textsuperscript{-1}, then cooled to $T_{\text{start oxidation}} = 1000$ °C with $P_{\text{solar}} = 0$ kW where oxidation was performed with $\dot{V}_{\text{CO}_2} = 7$ L min\textsuperscript{-1} until $T_{\text{end oxidation}} = 600$ °C.

Figure 3.6 (b) shows the specific amounts of O\textsubscript{2} and CO released, the reduction time duration, and $\eta_{\text{solar-to-fuel}}$ for the redox cycles. The O\textsubscript{2} and CO yields increased linearly by 10 \% by increasing $\dot{V}_{\text{Ar}}$ from 4 to 13 L min\textsuperscript{-1}. This is attributed to the lower $p_{\text{O}_2}$ resulting from stronger dilution of released O\textsubscript{2}, which in turn increased the reduction extent. Higher $\delta$ led to higher peak CO rates during the oxidation step, reaching 0.57 mL min\textsuperscript{-1} g\textsuperscript{-1}CeO\textsubscript{2} at $\dot{V}_{\text{Ar}} = 13$ L min\textsuperscript{-1} vs. 0.41 mL min\textsuperscript{-1} g\textsuperscript{-1}CeO\textsubscript{2} at $\dot{V}_{\text{Ar}} = 4$ L min\textsuperscript{-1}. On the other hand, higher $\dot{V}_{\text{Ar}}$ increased the reduction time and thereby the solar energy input integrated over the cycle, $Q_{\text{solar}}$, because more energy was required to heat the inert gas to the reaction temperature. Heating the Ar stream from 25 to 1450 °C (end of reduction step) consumes 3.0 \% of $P_{\text{solar}}$ at $\dot{V}_{\text{Ar}} = 4$ L min\textsuperscript{-1} and 9.7 \% of $P_{\text{solar}}$ at $\dot{V}_{\text{Ar}} = 13$ L min\textsuperscript{-1}, but this energy penalty can be drastically decreased by recovering the sensible heat of the outlet gas flows and using it to preheat the inlet gas flows (not accomplished in this study). Because of opposing effects when increasing $\dot{V}_{\text{Ar}}$, namely higher fuel yield vis-à-vis higher $Q_{\text{solar}}$ and energy for Ar/O\textsubscript{2} separation, we observed a maximum for $\eta_{\text{solar-to-fuel}}$ at $\dot{V}_{\text{Ar}} = 10$ L min\textsuperscript{-1} under the given operating conditions. These results indicate that efficiency gains by optimizing the inert gas flow rate are limited, thus alternative means of reducing $p_{\text{O}_2}$, such as vacuum operation, should be considered in the future.

\textsuperscript{§} per unit mass of ceria
Figure 3.6. (a) Nominal solar reactor temperature and specific $O_2$ and CO evolution rates during CO$_2$-splitting cycles for various Ar flow rates. (b) Total specific $O_2$ and CO evolution, reduction time duration, and solar-to-fuel energy conversion efficiency of these cycles vs. the Ar mass flow rate. Experimental conditions: $P_{solar} = 2.95$ kW, $T_{reduction} = 1450$ °C, $T_{start~oxidation} = 1000$ °C, $T_{end~oxidation} = 600$ °C, and $V_{CO2} = 7$ L min$^{-1}$. 
**Reduction temperature** – Besides $p_{O_2}$, the reduction temperature determines $\delta$ and, thus, the thermodynamic maximum amounts of $H_2$ and CO that can be produced per cycle. Higher $T_{\text{reduction}}$ implies higher $\delta$ but, on the other hand, it also induces higher re-radiation losses through the cavity’s aperture, resulting in an opposite effect on $\eta_{\text{solar-to-fuel}}$. Besides, high $T_{\text{reduction}}$ can be detrimental on the material morphology because of sintering and sublimation. Thus, choosing the optimal $T_{\text{reduction}}$ for maximizing $\eta_{\text{solar-to-fuel}}$ is multifaceted. Figure 3.7 (a) shows the nominal solar reactor temperature and specific $O_2$ and CO evolution rates of redox cycles for various peak reduction temperatures $T_{\text{reduction}} = 1450, 1500$ and $1550$ °C at $P_{\text{solar}} = 3.5$ kW, fixed oxidation starting temperature of $T_{\text{start oxidation}} = 1000$ °C and a fixed oxidation end temperature of $T_{\text{end oxidation}} = 600$ °C. The Ar and CO$_2$ flows during reduction and oxidation were constant at $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$ and $\dot{V}_{\text{CO}_2} = 7$ L min$^{-1}$, respectively. Figure 3.7 (b) shows the specific amount of $O_2$ and CO released, the reduction time, and $\eta_{\text{solar-to-fuel}}$ of these cycles. Increasing the reduction temperature from 1450 to 1550 °C resulted in an increase of the fuel yield by 68%, while the reduction time and $Q_{\text{solar}}$ increased by 34% due to the larger temperature swing. The increase in fuel yield overweighed the increase in $Q_{\text{solar}}$ because of the non-linear behavior of $\delta$ vs. $T^{50}$, which led to a monotonic increase in $\eta_{\text{solar-to-fuel}}$ with $T_{\text{reduction}}$ in the considered range. Although higher $\eta_{\text{solar-to-fuel}}$ might be achieved at higher $T_{\text{reduction}}$, we limited $T_{\text{reduction}}$ to 1500 °C in the subsequent experiments to avoid degradation of the ceria structure.
Figure 3.7. (a) Nominal solar reactor temperature and specific $O_2$ and CO evolution rates during $CO_2$-splitting cycles for various reduction temperatures. (b) total specific $O_2$ and CO evolution, reduction time duration, and solar-to-fuel energy conversion efficiency of these cycles vs. the reduction temperature for varying $T_{\text{reduction}}$. Experimental conditions: $P_{\text{solar}} = 3.5 \text{ kW}$, $\dot{V}_{\text{Ar}} = 7 \text{ L min}^{-1}$, $T_{\text{start oxidation}} = 1000 \text{ °C}$, $T_{\text{end oxidation}} = 600 \text{ °C}$, and $\dot{V}_{\text{CO}_2} = 7 \text{ L min}^{-1}$.
Solar radiative power input – To assess the sensitivity of the process to variations in the direct normal solar irradiation, we conducted CO\textsubscript{2}-splitting cycles at various $P_{\text{solar}}$ in the range 2.4 – 3.5 kW, corresponding to mean solar concentration ratios $C_{\text{solar}}$ at the aperture in the range 1890 – 2750 suns. Figure 3.8 (a) shows the nominal solar reactor temperature and specific O\textsubscript{2} and CO evolution rates for $P_{\text{solar}} = 2.4, 2.9, \text{ and } 3.5\ kW$, with $T_{\text{reduction}} = 1450$, $T_{\text{start oxidation}} = 1000\ ^\circ\text{C}$, $T_{\text{end oxidation}} = 600\ ^\circ\text{C}$ and constant gas flow rates of $\dot{V}_{\text{Ar}} = 7\ L\ \text{min}^{-1}$ and $\dot{V}_{\text{CO2}} = 7\ L\ \text{min}^{-1}$.

Figure 3.8 (b) shows the specific amounts of O\textsubscript{2} and CO released, the reduction time duration, and $\eta_{\text{solar-to-fuel}}$ of these cycles. The reduction time duration decreased significantly from 38 min at $P_{\text{solar}} = 2.4\ kW$ to 14 min at $P_{\text{solar}} = 3.5\ kW$ while only a minor increase in fuel yield was observed at higher $P_{\text{solar}}$ because the fixed peak reduction temperature limits $\delta$ in equilibrium. Consequently, $\eta_{\text{solar-to-fuel}}$ increased with $P_{\text{solar}}$ from 0.9 % at $P_{\text{solar}} = 2.4\ kW$ to 1.9 % at $P_{\text{solar}} = 3.5\ kW$, which is attributed to smaller heat losses during the shorter cycle time durations. For the cycle at $P_{\text{solar}} = 3.5\ kW$ (corresponding to $C_{\text{solar}} = 2750$), $Q_{\text{solar}}$ was 46% lower than that for the cycle at $P_{\text{solar}} = 2.4\ kW$ (corresponding to $C_{\text{solar}} = 1890$). Thus, fast heating at high $C_{\text{solar}}$ is affecting positively $\eta_{\text{solar-to-fuel}}$. Note however that high solar concentration requires more precise – and thus more expensive – concentrating optics or, alternatively, capturing only the high-flux solar radiation which decreases the optical efficiency of the concentrating system (not considered in this study).

** The solar concentration ratio $C_{\text{solar}}$ is defined as $C_{\text{solar}} = P_{\text{solar}}/(I \cdot A)$, where $P_{\text{solar}}$ is the solar radiative power intercepted by the aperture of area $A$, normalized to the direct normal solar irradiation $I$. $C_{\text{solar}}$ is often expressed in units of “suns” when normalized to $I = 1\ kW\ m^2$. 
Figure 3.8. (a) Nominal solar reactor temperature and specific O$_2$ and CO evolution rates during CO$_2$-splitting cycles for various solar radiative power inputs during reduction. (b) total specific O$_2$ and CO evolution, reduction time duration, and solar-to-fuel energy conversion efficiency of these cycles vs. the solar radiative power input during reduction. Experimental conditions: $T_{\text{reduction}} = 1450$ °C, $V_{\text{Ar}} = 7$ L min$^{-1}$, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C, and $V_{\text{CO}_2} = 7$ L min$^{-1}$. 
**CO$_2$ flow rate** – A high conversion of the reactant gases CO$_2$/H$_2$O to CO/H$_2$ is desirable because it simplifies the downstream processing of the product gas stream such as CO$_2$ removal or syngas compression. These might become relevant for the overall process efficiency and cost, especially when the CO$_2$ conversion is low. The oxidant flow rate affects its residence time in the reactor and thereby also its conversion. **Figure 3.9** shows the specific CO evolution rate vs. time for three CO$_2$-splitting cycles at $\dot{V}_{\text{CO}_2} = 1$, 4, and 7 L min$^{-1}$. Experimental conditions were: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1450$ °C, $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C. The inset in Figure 3.9 shows the average conversion of CO$_2$ to CO. Higher CO$_2$ flow rates led to higher CO evolution rates and, consequently, shorter oxidation times because of the higher CO$_2$:CO molar ratio maintained in the proximity of the RPC. In contrast and as expected, higher $\dot{V}_{\text{CO}_2}$ resulted in a lower CO$_2$ conversion – only 5% at $\dot{V}_{\text{CO}_2} = 7$ L min$^{-1}$ vis-a-vis 24% at $\dot{V}_{\text{CO}_2} = 1$ L min$^{-1}$, attributed to the shorter residence time of CO$_2$ as it flows across the RPC.

**Figure 3.9.** Specific CO evolution rate during CO$_2$-splitting cycles for various CO$_2$ flow rates. The insert shows the cycle’s averaged CO$_2$-to-CO conversion vs. the CO$_2$ flow rate. Experimental conditions: $P_{\text{solar}} = 3.5$ kW, $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$, $T_{\text{reduction}} = 1450$ °C, $T_{\text{start oxidation}} = 1000$ °C, and $T_{\text{end oxidation}} = 600$ °C.
**Oxidation temperature** – The temperature during the oxidation step affects the overall cycle performance in multiple ways. A high end of oxidation temperature $T_{\text{end oxidation}}$ and thus small temperature swing between reduction and oxidation is desirable to reduce $Q_{\text{solar}}$, as less solar energy needs to be invested during every cycle to heat the RPC from $T_{\text{oxidation}}$ to $T_{\text{reduction}}$. However, at the same time, the oxidation temperature affects both the thermodynamics and kinetics of the reaction (Equations 1.6 and 1.7). The situation is complicated by the spatially and temporally-varying temperature, gas concentrations, and $\delta$ across the RPC.

**Figure 3.10** shows the specific CO rate (left y-axis) and CO concentration (right y-axis) as a function of $T_{\text{oxidation}}$ during CO$_2$-splitting cycles at $\dot{V}_{\text{CO}_2} = 7$ L min$^{-1}$ for $T_{\text{start oxidation}} = 800, 1000,$ and $1200 \, ^\circ$C (solid lines) and the corresponding curves for the calculated thermodynamic limit (dashed lines). The time scale is indicated in the top x-axis. For the reduction step experimental conditions were kept the same: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1450 \, ^\circ$C, $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$. Higher $T_{\text{start oxidation}}$ led to lower CO rates and lower CO$_2$ conversions. For $T_{\text{start oxidation}} = 1200 \, ^\circ$C, the CO concentration initially increased rapidly to about 1% and then gradually to its peak value of 7% at 950 $^\circ$C before gradually decreasing to 1 % at 680 $^\circ$C. Interestingly, for $T_{\text{start oxidation}} = 1000 \, ^\circ$C, the peak and completion occurred at the same temperatures. We attributed this behavior to a thermodynamic limitation of CO evolution, as confirmed by equilibrium compositions computed for the measured temperature during oxidation and $\delta$ achieved during the reduction step.
Figure 3.10. Specific CO rate (left y-axis) and CO concentration (right y-axis) as a function of the oxidation temperature during a CO\textsubscript{2}-splitting cycle at various \( T_{\text{start oxidation}} \) (solid lines) and the corresponding curves for the calculated thermodynamic limit (dashed lines). The time scale is indicated in the top x-axis. Experimental conditions: \( P_{\text{solar}} = 3.5 \text{ kW} \), \( \dot{V}_{\text{Ar}} = 7 \text{ L min}^{-1} \), \( T_{\text{reduction}} = 1450 \degree \text{C} \), \( T_{\text{end oxidation}} = 600 \degree \text{C} \), and \( \dot{V}_{\text{CO}_2} = 7 \text{ L min}^{-1} \).

Temperature and gas concentrations were assumed to be uniform throughout the cavity and the equilibrium \( P_{\text{O}_2} \) was calculated in each time step from nonstoichiometry data of Panlener \textit{et al.}\textsuperscript{50} Given \( P_{\text{O}_2} \), \( P_{\text{CO}} \) was calculated according to:

\[
P_{\text{CO}} = \frac{P_{\text{CO}_2}}{K_f \cdot P_{\text{O}_2}^{0.5}} \tag{3.10}
\]

where \( K_f \) is the equilibrium constant for the \( \text{CO}_2 \) formation reaction, obtained from NIST-JANAF thermochemical tables. The effect of direct thermolysis of \( \text{CO}_2 \), i.e. \( \text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2 \) on the \( \text{CO}_2:\text{CO} \) molar ratio was neglected since, at \( T < 1200 \degree \text{C} \), its equilibrium \( P_{\text{CO}} \) is about 2 orders of magnitude lower than that of Equation 1.7. The dashed
curves in Figure 3.10 show the calculated thermodynamic limit of CO evolution for the three experimentally studied cycles. The CO concentration obtained experimentally at above 1000 °C was on the order of the thermodynamic limit, whereas it was significantly lower at lower temperature, indicating a kinetic or mass transport limitation. The difference between the thermodynamic limit curves and the experimentally measured ones are presumably due to the non-uniformity of temperatures and CO concentrations within the RPC, which was not captured in the model. These results further imply that low $T_{\text{start oxidation}}$ are necessary to achieve high CO$_2$ conversion, even when low flow rates (long residence times) are applied.

**Co-splitting H$_2$O and CO$_2$** – Most experiments were performed solely with CO$_2$ as oxidant, whereas the co-feeding of H$_2$O and CO$_2$ for the co-production of H$_2$ and CO (syngas) offers economic advantages because of the elimination of the water-gas-shift reaction.$^{112}$ Further, the syngas’s economic value decreases with the content of unreacted CO$_2$ and inert Ar as it requires additional separation steps and/or handling of unnecessarily large gas streams. Based on the findings discussed above, we therefore performed CO$_2$ and H$_2$O co-splitting cycles at a low $T_{\text{start oxidation}}$ and with a low oxidant flow rate to maximize conversion. Figure 3.11 shows the nominal solar reactor temperature and the O$_2$, H$_2$ and CO concentrations of such a redox cycle. Experimental conditions were: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1450$ °C, $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$, $T_{\text{start oxidation}} = 750$ °C, $\dot{V}_{\text{CO2}} = 0.45$ L min$^{-1}$, $\dot{V}_{\text{H2O}} = 2.5$ L min$^{-1}$. The cycle-averaged product gas composition, after removal of excess H$_2$O, was 32.4 % H$_2$, 16.3 % CO, 34.3 % CO$_2$ and 17 % Ar, corresponding to a H$_2$:CO molar ratio of 2 and a syngas concentration of 48.7 %. The results from the previous chapter showed that syngas of similar composition can be directly processed to liquid fuels via FT-synthesis.$^{125}$ Alternatively, CO$_2$ could be separated prior to further processing with a relatively low energy penalty as the theoretic minimum separation work is approximately 1% of the syngas’s heating value.
Figure 3.11. Nominal solar reactor temperature and \( \text{O}_2 \), \( \text{CO} \) and \( \text{H}_2 \) concentrations as a function of time during the simultaneous co-splitting of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). Experimental conditions: \( P_{\text{sol}} = 3.5 \text{ kW}, T_{\text{reduction}} = 1450 \text{ °C}, \dot{V}_{\text{Ar}} = 7 \text{ L min}^{-1}, T_{\text{start oxidation}} = 750 \text{ °C}, T_{\text{end oxidation}} = 550 \text{ °C}, \dot{V}_{\text{CO}_2} = 0.45 \text{ L min}^{-1}, \) and \( \dot{V}_{\text{H}_2\text{O}} = 2.5 \text{ L min}^{-1} \).

Optimized cycles - Based on the parametric study, we selected the operating conditions to maximize \( \eta_{\text{solar-to-fuel}} \) while maintaining stable operation of the solar reactor without degradation of the RPC over time. Thus, the reduction temperature was limited to a maximum of 1500 °C and the oxidation step was terminated before completion to maximize efficiency and increase the \( \text{CO}_2 \) conversion. Figure 3.12 shows the nominal solar reactor temperature and the specific \( \text{O}_2 \) and \( \text{CO} \) evolution rates of five consecutive cycles at \( P_{\text{sol}} = 4.1 \text{ kW} \) with \( T_{\text{reduction}} = 1500 \text{ °C}, \dot{V}_{\text{Ar}} = 7 \text{ L min}^{-1}, T_{\text{start oxidation}} = 1000 \text{ °C}, T_{\text{end oxidation}} = 700 \text{ °C}, \dot{V}_{\text{CO}_2} = 7 \text{ L min}^{-1} \). Stable operation was observed, attributed to the good mechanical stability of the infiltrated DS-RPC structure as well as to the improved cavity geometry and flow configuration of the gen-2 solar reactor that created more uniform temperature distributions, eliminated hot spots, and effectively protected the solar reactor’s window from condensation of sublimated ceria. Based on cycles #2-5, \( \eta_{\text{solar-to-fuel}} \) was 2.58 %, with a standard deviation of 0.0125 % between cycles.
Figure 3.12. Nominal solar reactor temperature and specific O\textsubscript{2} and CO evolution rates as a function of time during 5 consecutive CO\textsubscript{2}-splitting cycles at optimized experimental conditions: $P_{\text{solar}} = 4.1$ kW, $T_{\text{reduction}} = 1500$ °C, $V_{\text{Ar}} = 7$ L min\textsuperscript{-1}, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 700$ °C, and $V_{\text{CO}_2} = 7$ L min\textsuperscript{-1}.

Comparison gen-1 vs. gen-2 – Figure 3.13 shows the nominal solar reactor temperature and O\textsubscript{2} and CO evolution rates during CO\textsubscript{2}-splitting redox cycles obtained with the gen-2 (solid lines) and gen-1 solar reactors (dashed lines; Chapter 2) for the same solar power input and optimized conditions for both solar reactors. A summary of the operating conditions and results are listed in Table 3.2. During the reduction step at $T < 1400$ °C, higher heating rates with a peak of 194 °C min\textsuperscript{-1} were observed for gen-1 versus 127 °C min\textsuperscript{-1} for gen-2. This is explained by the 82% higher CeO\textsubscript{2} mass loading and the lower peak radiative flux on the RPC for gen-2. Nevertheless, at $T > 1400$ °C, the heating rate of gen-2 surpassed that of the gen-1 reactor due to lower heat losses and reached 35 °C min\textsuperscript{-1} (62% higher) at 1500 °C. The peak O\textsubscript{2} evolution rates were 0.22 L min\textsuperscript{-1} and 0.51 L min\textsuperscript{-1} for gen-1 and gen-2, respectively, mainly due to the increased ceria mass loading and increased heating rate. After reduction, the cooling proceeded slower for gen-2 due to lower heat losses, which led to a longer cycle duration despite the shorter reduction step. Slow cool-down is
beneficial for the recovery of the sensible heat of the solids during the temperature-swing, but no attempt was undertaken for heat recovery in this Chapter. The CO evolution rates were similar between both solar reactors because of the same μm-sized porosity of the RPC structure. Despite more moderate operating conditions, $\eta_{\text{solar-to-fuel}}$ was increased by 50%, from 1.72% for gen-1 to 2.58% for gen-2.

**Figure 3.13.** Nominal solar reactor temperatures and specific O$_2$ and CO evolution rates as a function of time during a CO$_2$-splitting cycle performed with the gen-1 solar reactor (dashed lines) and the gen-2 solar reactor (solid lines) with same $P_{\text{solar}}$ and optimized experimental conditions given in Table 3.2).
Table 3.2. Solar experimental conditions and results for a CO$_2$ splitting redox cycle conducted with the gen-1 and with the gen-2 reactor at the same $P_{\text{solar}}$.

<table>
<thead>
<tr>
<th>Solar reactor</th>
<th>gen-1</th>
<th>gen-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria RPC mass (g)</td>
<td>948</td>
<td>1728</td>
</tr>
<tr>
<td>Solar radiative power input, $P_{\text{solar}}$ (kW)</td>
<td>3.8 (at aperture)††</td>
<td>4.1 (at window)</td>
</tr>
<tr>
<td>Reduction temperature, $T_{\text{reduction}}$ (°C)</td>
<td>1576</td>
<td>1500</td>
</tr>
<tr>
<td>Start of oxidation temperature $T_{\text{start oxidation}}$ (°C)</td>
<td>1320</td>
<td>1000</td>
</tr>
<tr>
<td>End of oxidation temperature $T_{\text{end oxidation}}$ (°C)</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Ar flow rate reduction, $\dot{V}_{\text{Ar}}$ (L min$^{-1}$)</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>CO$<em>2$ flow rate during oxidation, $\dot{V}</em>{\text{CO}_2}$ (L min$^{-1}$)</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Reduction duration, $t_{\text{reduction}}$ (min)</td>
<td>15.0</td>
<td>10.6</td>
</tr>
<tr>
<td>Mean heating rate (°C min$^{-1}$)</td>
<td>59</td>
<td>76</td>
</tr>
<tr>
<td>Peak heating rate (°C min$^{-1}$)</td>
<td>194</td>
<td>127</td>
</tr>
<tr>
<td>Peak specific O$_2$ evolution rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>0.26±0.05</td>
<td>0.30±0.03</td>
</tr>
<tr>
<td>Peak O$_2$ evolution rate (L min$^{-1}$)</td>
<td>0.25±0.05</td>
<td>0.51±0.05</td>
</tr>
<tr>
<td>Absolute O$_2$ evolution (L)</td>
<td>2.39±0.08</td>
<td>2.85±0.06</td>
</tr>
<tr>
<td>Peak specific CO release rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>1.13±0.11</td>
<td>0.68±0.08</td>
</tr>
<tr>
<td>Peak CO release rate (L min$^{-1}$)</td>
<td>1.07±0.10</td>
<td>1.17±0.13</td>
</tr>
<tr>
<td>Absolute CO release (L)</td>
<td>4.76±0.30</td>
<td>6.10±0.67</td>
</tr>
<tr>
<td>Molar ratio CO:O$_2$ (-)</td>
<td>1.99±0.19</td>
<td>2.14±0.28</td>
</tr>
<tr>
<td>Solar-to-fuel energy conversion efficiency, $\eta_{\text{solar-to-fuel}}$ (%)</td>
<td>1.72±0.11</td>
<td>2.58±0.06</td>
</tr>
</tbody>
</table>

†† For the efficiency calculation of the gen-1 reactor the window losses were not included and $P_{\text{solar}} = 3.8$ kW was used. $P_{\text{solar}}$ was the same for both reactors when including the window losses in both cases.
Figure 3.14 shows the temperatures measured at the indicated locations within the gen-1 and gen-2 reactors to directly compare the temperature distribution. The improved cavity geometry of the gen-2 design significantly decreased the temperature difference between the front and the back of the cavity which was 95 and 17 °C in the gen-1 and gen-2 reactor, respectively.

![Figure 3.14](image)

**Figure 3.14.** Temperatures measured during thermal reduction and cooling within the gen-1 and gen-2 reactors at the indicated locations.

**Nonstoichiometry distribution** – To further assess the temperature distribution with a higher spatial resolution than from the thermocouple measurements, the distribution of $\delta$ after thermal reduction was measured. It allows to draw qualitative conclusions on the temperature distribution throughout the ceria RPC during reduction as $T$ and $\delta$ are coupled through thermodynamics. Figure 3.15 shows $\delta$ at the indicated locations measured after thermal
reduction at $P_{\text{solar}} = 2.9 \text{ kW}$, $T_{\text{reduction}} = 1554 \, ^\circ\text{C}$ with $\dot{V}_{\text{Ar}} = 7 \, \text{L min}^{-1}$. Note that the values represent averaged values over the indicated areas (sample thickness = 2.5 cm). The results indicate differences in nonstoichiometry – and therefore in also temperature – both in circumferential and in radial directions. The locations of maximum $\delta$ and $T$ in circumferential direction are in agreement with the location of the spots of the single xenon arc lamps of the HFSS used in this experiment (the locations of the spots are indicated in Figure 3.15). Assuming a constant $p_{O_2} = 2.1 \cdot 10^{-2} \, \text{bar}$ within the reactor cavity and extrapolating available ceria nonstoichiometry data, approximate temperature differences can be estimated from the nonstoichiometry distribution.$^{50, 83}$ In circumferential direction the maximum temperature difference between the samples was approximately 50 °C. Note that these gradients result from the experimental setup (with single lamps) and are not expected in an on-sun application. Gradients in radial direction were larger and corresponded to a temperature difference of approximately 80 °C between the irradiated side and the back side of the RPC. Note that this difference is an average between the front and the back half of the RPC, hence temperature differences between the innermost irradiated surface layer and the backside are expected to be even larger. The gradient arises because more radiation is absorbed at the irradiated surface of the RPC than towards the back side and reveals further optimization potential of the RPC pore structure to tune the optical thickness for obtaining a more uniform temperature distribution in radial direction.
Figure 3.15. Experimentally measured distribution of ceria nonstoichiometry in the solar reactor after thermal reduction. Experimental conditions: $P_{\text{solar}} = 2.9$ kW, $T_{\text{reduction}} = 1554$ °C and $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$.
3.4 Summary and Conclusions

The design optimization and experimental characterization of an improved solar reactor for thermochemical splitting of H$_2$O and CO$_2$ via a ceria-based redox cycle was presented. The RPC structure featured dual-scale porosity and infiltrated struts. The variation of the Ar flow rate during the reduction step revealed a weak influence on $\eta_{\text{solar-to-fuel}}$, and thus other strategies to reduce $p_{O_2}$ should be considered, e.g. vacuum pressures. On the other hand – as expected – the reduction temperature was found to have a strong influence on $\eta_{\text{solar-to-fuel}}$, with higher temperatures being beneficial, but maximum temperatures are limited to about 1500°C due to the RPC degradation. During oxidation at above 1000 °C, the CO$_2$ conversion was close to the thermodynamic limit. Stable operation of a simple and robust solar reactor for producing high-quality syngas suitable for gas-to-liquid processing with a $\eta_{\text{solar-to-fuel}}$ for CO$_2$-splitting of 2.6% was demonstrated.
In this chapter, combined vacuum-temperature swing operation of the gen-2 prototype reactor is investigated experimentally. During the endothermic reduction step, the reactor was evacuated to pressures in the range 100-10 mbar while heated with solar radiative power inputs in the range 2.9-4.1 kW to nominal reactor temperatures of 1450-1500 °C. Subsequent oxidation with CO\textsubscript{2} to produce CO was performed at atmospheric pressure at temperatures in the range 600-1000 °C. The fuel yield during vacuum cycles at 10 mbar was 73 % higher compared to cycles at atmospheric pressure with inert gas purging due to a 10-fold lower oxygen partial pressure during the thermal reduction. The solar-to-fuel energy conversion efficiency was 5.25 % which is roughly two times greater compared to cycles where inert gas purging was applied using the same reactor.

‡‡ Material in this chapter will be submitted for publication as: D. Marxer, P. Furler, M. Takacs and A. Steinfeld, “Solar thermochemical splitting of CO\textsubscript{2} into separate streams of CO and O\textsubscript{2} with high selectivity, stability, conversion, and efficiency.”
4.1 Motivation

The oxygen partial pressure \( (p_{O_2}) \) during the thermal reduction step (Equation 1.5) directly influences the oxygen exchange capacity of ceria and thereby the fuel yield per cycle. Typically a flow of inert gas (Ar, N\(_2\), He) is used to reduce \( p_{O_2} \) during reduction. The energy required for production and for heating of the flow of inert gas to the reduction temperature can have a significant impact on the energy budget of the process. The results in the previous Chapter 3 revealed that \( p_{O_2} \) below \( 10^{-2} \) atm could not be achieved without excessive heat removal from the process by the necessary high sweep gas flow rates. The energy penalty for heating of the inert gas could be lowered - but not avoided - by recovering the sensible heat from the gas stream leaving the reactor.

An alternative method to decrease \( p_{O_2} \) during the reduction step is to reduce the total pressure in the reactor (vacuum operation) and thereby limit the maximum \( p_{O_2} \) to the total pressure. Recent thermodynamic studies indicate that vacuum pumping is more energy efficient compared to inert gas separation, and as a result the expected solar-to-fuel energy conversion efficiency is higher. As an added benefit, spatial gradients of \( p_{O_2} \) in the reactor are not expected under vacuum as pressure gradients equilibrate rapidly. Furthermore, the gas phase thermal conductivity under vacuum is very low, which has the potential to lower conduction heat losses from the reactor chamber. In contrast to atmospheric pressure operation, the heat removed from the reactor does not increase upon lowering \( p_{O_2} \) but the heat losses might even decrease. Also, inert gas impurities in the produced syngas that were observed experimentally at atmospheric pressure operation could be avoided. On the other hand, an evident challenge of vacuum operation with a directly irradiated reactor is the need for a transparent window that withstands pressure differences of \(~1 \) bar.
4.2 Materials and Methods

Solar reactor design – The solar reactor design was described in the previous Chapter in Section 3.2. Two different quartz window designs were investigated during vacuum operation. In design 1, shown in Figure 4.1 (a), the reactor front is sealed by an 11 cm-diameter, 4 mm-thick clear fused, flat quartz disk window (GVB GmbH, EN08NB). The second window design is shown in Figure 4.1 (b); it consists of a dome window with the shape of a spherical cap with curvature radius 140 mm, cap angle 65° and a thickness of 4 mm (Heraeus GmbH, HOQ310). The cap angle is chosen < 90° (half sphere) to enable secure clamping of the window also in case of slight overpressures in the reactor.

When using window option 1, reacting gases were injected through 6 tangential inlet ports behind the window with 30° inclination to the radial direction. For window option 2, gases were injected parallel to the window through 3 inlet ports with a 30° tangential component. A fraction of the gases was injected through 4 inlet ports behind the aperture with both window options. Product gases exited through 5 outlet ports at the rear plate. The flow configuration for both window options was chosen based on CFD simulations (Section 3.2) to avoid back-flow from the hot reactor cavity to the reactor front.
Figure 4.1. (a) Schematic of the vacuum reactor with a flat quartz disk window. (b) Reactor with a quartz dome window with the shape of a spherical cap, mounted on the reactor. (c) Experimental setup for vacuum pressure operation during reduction step and atmospheric pressure during the oxidation step.
**Experimental setup** – A schematic of the setup for vacuum experiments is shown in Figure 4.1 (e). Argon (99.996 % purity) and CO\textsubscript{2} (99.998 % purity) flow rates were regulated by electronic mass flow controllers (Bronkhorst F-201 C). The ambient air flow rate was regulated by a manual mass flow controller driven by the pressure difference between reactor pressure, $p_{\text{reactor}}$, and atmospheric pressure, $p_{\text{atm}}$, while $p_{\text{reactor}} < p_{\text{atm}}$. The reactor pressure was monitored by a capacitance diaphragm vacuum gauge (THERMOVAC TTR 101). A dry vacuum pump (Adixen ACP 15) was attached to the outlet of the reactor and could be detached by an electro-pneumatic valve (Pfeiffer AVC 025 PA) and bypassed for the oxidation step via a magnet valve (SMC VX214FGAXB). Soft evacuation of the reactor to avoid dust entrainment from the insulation was achieved with an electronically controlled variable cross-section magnet valve (SMC PVQ 33-6G-40-01F) in parallel to the electro-pneumatic valve. Product gas composition was monitored downstream of the pump (reduction step) or bypass (oxidation step) by gas chromatography (Varian 490), supplemented by an electrochemical sensor for O\textsubscript{2} (Siemens Ultramat 23) and infrared-based detectors for CO and CO\textsubscript{2} (Siemens Ultramat 23).

Experimentation was performed at the HFSS of ETH Zurich, as described in Section 2.1.

Figure 4.2 schematically illustrates the 3 different operating modes that were investigated in this chapter. In operation mode #1, the reactor was heated by $P_{\text{solar}} = 2.4 - 4.1$ kW to the desired reduction temperature $T_{\text{reduction}}$ in the range 1450-1550 °C while purging with Ar flow rates $\dot{V}_{\text{Ar}}$ ranging from 0.625 to 5 L min\textsuperscript{-1} while simultaneously maintaining vacuum pressures within the reactor. Following reduction, the HFSS was turned off ($P_{\text{solar}} = 0$) and 1 minute later, the vacuum pump was decoupled from the reactor, and the reactor filled to $p_{\text{amb}}$ with Ar. Upon cooling to the desired oxidation temperature $T_{\text{start oxidation}}$ in the range 700-1000 °C, oxidation was performed by injecting CO\textsubscript{2} with flow rates ranging from 3 to 7 L min\textsuperscript{-1}. 
Figure 4.2. Temperature, pressure and O\textsubscript{2} and CO evolution rates of an arbitrary CO\textsubscript{2} splitting cycle and three different operation modes indicated. In operation mode #1 the reactor is evacuated during thermal reduction while purged with Ar, and filled with Ar after the reduction step. In mode #2 the reactor is filled with CO\textsubscript{2} after reduction. In mode #3, ambient air is used for purging instead of Ar.

Operation mode #2 was designed to improve the CO\textsubscript{2} conversion and avoid Ar impurities in the produced fuel gas, therefore the reactor was directly filled with CO\textsubscript{2} after the reduction step. Upon reaching $p_{\text{amb}}$, the reactor was sealed by closing all valves. When the reactor had cooled to the desired $T_{\text{start oxidation}}$, the bypass valve was opened and CO\textsubscript{2} injected to purge out already produced CO and continue oxidation. In operation mode #3 ambient air was used instead of Ar during the reduction step.

Active cooling of the reactor after thermal reduction was accomplished with N\textsubscript{2} (99.999 % purity) injected to the gas inlet nozzles behind the window at $\dot{V}_{\text{N2}} = 100$ L min$^{-1}$ at room temperature. The N\textsubscript{2} temperature at the outlet of the reactor was monitored with a B-type thermocouple.
**RPC synthesis** – The same infiltrated DS-RPC structure as in Chapter 3 was used (for the manufacturing procedure refer to Section 3.2). The total CeO$_2$ RPC mass load was 1728 g.

**Energy conversion efficiency** - The thermochemical performance of the solar reactor is given by the solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$, which for vacuum operation 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)

Where the energy stored in the fuel, $Q_{\text{fuel}}$, is defined as:

$$Q_{\text{fuel}} = \Delta H_{\text{fuel}} \int r_{\text{fuel}} dt$$  \hspace{1cm} (4.2)

With the heating value of the fuel produced, $\Delta H_{\text{fuel}}$, and the molar rate of fuel produced, $r_{\text{fuel}}$. The solar energy input to the cycle, $Q_{\text{solar}}$, is defined as:

$$Q_{\text{solar}} = \int P_{\text{solar}} dt$$  \hspace{1cm} (4.3)

Where $P_{\text{solar}}$ is the radiative power input through the reactor’s aperture divided by the total transmittance of the quartz window (assumed 93.2 %)$^{126}$. The vacuum pumping energy, $Q_{\text{pump}}$, 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)$^4, 53, 128$, and a pressure-dependent vacuum pump efficiency, $\eta_{\text{pump}}$, according to:

$$Q_{\text{pump}} = \frac{1}{\eta_{\text{heat-to-work}} \cdot \eta_{\text{pump}} (P_{\text{reactor}})} \int \hat{n}(t) \cdot R \cdot T \cdot \ln \left( \frac{p_{\text{atm}}}{P_{\text{reactor}}(t)} \right) dt$$  \hspace{1cm} (4.4)

Where $\hat{n}(t)$ is the sum of the molar flow rates of: the gas injected to the reactor, the O$_2$ released by ceria, and the gas evacuated from the reactor during transient change of pressure. For $\eta_{\text{pump}}$ the following correlation was used:
\[ \eta_{\text{pump}} (p_{\text{reactor}}) = 0.07 \cdot \log \left( \frac{p_{\text{reactor}}}{p_{\text{atm}}} \right) + 0.4 \]  

(4.5)

The pressure dependent pump efficiency is based on the analysis of a multi-stage industrial vacuum pump arrangement from Pfeiffer vacuum and was derived by Brendelberger et al.\(^4\) Note that \(\eta_{\text{solar-to-fuel}}\) is not sensitive to small uncertainties in \(\eta_{\text{pump}}\) because \(Q_{\text{solar}} \gg Q_{\text{pump}}\) at the moderate vacuum pressure levels applied in this work.

Finally, the energy required for inert gas separation, \(Q_{\text{inert}}\), is defined as:

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

(4.6)

Where \(r_{\text{inert}}\) is the inert gas flow rate during reduction and \(E_{\text{inert}}\) is the work required for inert gas separation (assumed 20 kJ per mole of Ar).\(^96\)

**Energy balance calculations** – Re-radiation losses were calculated assuming a cavity emissivity = 1 and were integrated over the reduction step according to:

\[ Q_{\text{rerad}} = \int_{0}^{t_{\text{reduction}}} \sigma \cdot T(t)^4 \cdot A_{\text{aperture}} \, dt \]  

(4.7)

Where \(\sigma\) is the Stefan-Boltzmann constant, \(T(t)\) is the experimentally measured nominal reactor temperature and \(A_{\text{aperture}}\) is the aperture surface area. For the window absorption and reflection losses, a total transmissivity of the quartz window of 93.2% was assumed.\(^126\) The reflection losses from the cavity were calculated based on previously presented Monte-Carlo ray tracing simulations (Section 3.2). The energy required for the reduction of ceria was calculated using the measured released amount of oxygen and an average reduction enthalpy of 475 kJ per mole of atomic oxygen.\(^40\) For the sensible heating of ceria a heat capacity of 83 J mol\(^{-1}\) K\(^{-1}\) was used.\(^129\) Radiation
from the steel shell was calculated with the measured shell temperature assuming a shell emissivity of 0.6. Convection losses were calculated assuming natural convection from a horizontal cylinder and a vertical plate using the measured shell temperatures and according Nusselt correlations.\textsuperscript{116-117} Inert gas separation and vacuum pumping energy requirements were calculated according to Equations 4.6 and 4.4, respectively.

4.3 Experimental Results and Discussion

\textit{Combined purging and pumping} - Combinations of simultaneous Ar purging and vacuum pumping during the thermal reduction step (Equation 1.5) were investigated experimentally to assess if combinations of the two modes of lowering $p_{O2}$ are beneficial compared to either of the individual approaches. Figure 4.3 (a) shows the nominal solar reactor temperature, the total pressure in the reactor and the specific ox and CO evolution rates during CO$_2$-splitting redox cycles performed under vacuum pressure and with different Ar flow rates during the reduction step. The reactor was operated according to operation mode #1 in Figure 4.2; it was heated with $P_{\text{solar}} = 2.9$ kW to $T_{\text{reduction}} = 1450$ °C while continuously pumping vacuum and flowing Ar with $\dot{V}_{\text{Ar}} = 0.625 - 5$ L min$^{-1}$. After reduction, the reactor was filled with Ar to $p_{\text{atm}}$ while the reactor cooled down with $P_{\text{solar}} = 0$ kW. Upon reaching a fixed start of oxidation temperature of $T_{\text{start oxidation}} = 1000$ °C, oxidation was performed with $\dot{V}_{\text{CO2}} = 7$ L min$^{-1}$ until oxidation was terminated at $T_{\text{end oxidation}} = 600$ °C. Black arrows indicate the trends for increasing $\dot{V}_{\text{Ar}}$. Figure 4.3 (b) shows the influence of $\dot{V}_{\text{Ar}}$ on selected performance indicators of the cycles.

Increasing the Ar flow rate while simultaneously vacuum pumping was found to have exclusively detrimental effects on the process performance in the considered range. The Ar separation energy and the pumping energy increased linearly with $\dot{V}_{\text{Ar}}$. The reduction time

\textsuperscript{88} per unit mass of ceria
also increased slightly because of the higher amount of heat required to heat the inflowing argon to the reactor temperature. Interestingly, the amount of \( \text{O}_2 \) and \( \text{CO} \) produced was approximately constant with varying \( \dot{V}_{\text{Ar}} \) flow rate, which is in contrast to a variation of \( \dot{V}_{\text{Ar}} \) at atmospheric pressure where the fuel yield increased with \( \dot{V}_{\text{Ar}} \) (Section 3.3). Under vacuum, higher \( \dot{V}_{\text{Ar}} \) increased \( p_{\text{reactor}} \) due to the constant pumping speed applied and therefore the Ar flow did not help to lower \( p_{\text{O}_2} \) at the given conditions. These effects led to a decreased \( \eta_{\text{solar-to-fuel}} \) of 2.98 % at \( \dot{V}_{\text{Ar}} = 5 \text{ L min}^{-1} \) compared to 3.57 % at 0.625 L min\(^{-1}\). The results hence indicate that a combination of the two approaches to lower \( p_{\text{O}_2} \) is not desirable energetically and pure vacuum pumping would presumably be beneficial for \( \eta_{\text{solar-to-fuel}} \). We therefore also tested vacuum pumping with \( \dot{V}_{\text{Ar}} = 0 \text{ L min}^{-1} \), but this operating point was problematic since there was no defined flow through the reactor. As a consequence, natural convection transported hot gases containing small amounts of \( \text{CeO}_2(g) \) to the reactor front where it condensed on water cooled reactor parts and the quartz window. Operation under such conditions is not considered practical and therefore the data is not presented here. An alternative operating mode that avoids this problem and circumvents the need for Ar will be presented later.
Figure 4.3. (a) Nominal solar reactor temperature, reactor pressure and specific O₂ and CO evolution rates during CO₂ splitting cycles at vacuum pressure during reduction and varying $\dot{V}_{\text{Ar}}$. Black arrows indicate the trends for increasing $\dot{V}_{\text{Ar}}$. (b) Various process parameters vs. $\dot{V}_{\text{Ar}}$ of the cycles. Experimental conditions: $P_{\text{solar}} = 2.9 \text{ kW}$, $T_{\text{reduction}} = 1450 \degree \text{C}$, $T_{\text{start oxidation}} = 1000 \degree \text{C}$, $T_{\text{end oxidation}} = 600 \degree \text{C}$ and $\dot{V}_{\text{CO₂}} = 7 \text{ L min}^{-1}$. 
**Reduction pressure variation** – Besides $T_{\text{reduction}}$ and $\dot{V}_{\text{Ar}}$, the key operational parameter that directly affects the ceria nonstoichiometry and thereby the fuel yield per cycle is the total pressure in the reactor during the reduction step, hence we experimentally investigated pressures ranging from 100 to 10 mbar. Figure 4.4 (a) shows the nominal reactor temperatures and the O$_2$ and CO evolution rates of redox cycles conducted with different total pressures during the reduction step of 100, 50 and 10 mbar. The experimental conditions were: $P_{\text{solar}} = 3.5$ kW, $\dot{V}_{\text{Ar}} = 0.625$ L min$^{-1}$, $T_{\text{reduction}} = 1450$ °C, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C and $\dot{V}_{\text{CO2}} = 7$ L min$^{-1}$. Figure 4.4 (b) shows the amounts of O$_2$ and CO released, $Q_{\text{pump}}$ and $\eta_{\text{solar-to-fuel}}$. The reduction pressure had only a negligible influence on the thermal performance of the reactor in the considered range as visible by the mostly constant heating rates for varying pressure. Decreasing the total pressure by one order of magnitude from 100 to 10 mbar increased the O$_2$ yield by 71 % from 2.5 L to 4.3 L due to the lower $p_{\text{O2}}$. The increase in fuel yield was accompanied by an increase of the pumping work by a factor of 2.7, caused by multiple reasons. Higher molar flow rates had to be pumped at lower pressure due to the higher O$_2$ yield. Additionally, the thermodynamic pumping work increased according to Equation 4.4. On top of that, the vacuum pump efficiency decreased at low pressures due to increased internal backflow and friction losses in the pump (Equation 4.5).$^4$ Despite the increase in pump work, $\eta_{\text{solar-to-fuel}}$ increased steeply upon lowering the pressure from 2.4 % at 100 mbar to 4.2 % at 10 mbar due to the increased fuel yield. The trends indicate that even lower reduction pressures might be beneficial for efficiency, which however could not be tested with the vacuum components used in this work due to a limited pumping speed. The results are in agreement with thermodynamic studies that predict the highest efficiencies at lower pressures than investigated in the present work, whereas the reported values of optimal $p$ vary widely due to the large sensitivity towards the assumptions made.$^{4, 53, 56, 83, 128}$
**Figure 4.4.** (a) Nominal solar reactor temperature, reactor pressure and specific $\text{O}_2$ and CO evolution rates during $\text{CO}_2$ splitting cycles with varying reactor pressure during reduction. Black arrows indicate the trends for decreasing $p$. (b) $\text{O}_2$/CO evolution, $Q_{\text{pump}}$ and $\eta_{\text{solar-to-fuel}}$ of the cycles. Experimental conditions: $P_{\text{solar}} = 3.5 \text{ kW}$, $V_{\text{Ar}} = 0.625 \text{ L min}^{-1}$, $T_{\text{reduction}} = 1450 \degree \text{C}$, $T_{\text{start oxidation}} = 1000 \degree \text{C}$, $T_{\text{end oxidation}} = 600 \degree \text{C}$ and $V_{\text{CO2}} = 7 \text{ L min}^{-1}$.

**CO$_2$ conversion** – During the oxidation reaction, a high CO$_2$-to-CO conversion to decrease the CO$_2$ separation or compression work and a high $T_{\text{end oxidation}}$ to decrease the temperature swing of the process are desired. Results from the previous Chapter 3 indicated that, to achieve a high conversion, low oxidation temperatures to avoid thermodynamic limitations, high $\delta$, and high oxidant residence times are required. Based on these findings we designed experiments to improve conversion and avoid inert gas impurities, while keeping $T_{\text{end oxidation}}$ constant. To increase the residence time and avoid Ar impurities, the reactor was filled with CO$_2$ from 10 mbar to $p_{\text{atm}}$ after reduction (see Figure 4.2, operation mode #2) and $V_{\text{CO2}}$ was reduced. Higher $\delta$ was achieved by using vacuum during the reduction step to lower the $p_{\text{O2}}$. **Figure 4.5** shows the reactor temperature, pressure and O$_2$ and CO evolution rates and CO concentration for these cycles with different $T_{\text{start oxidation}}$ in the range 700 – 1000 °C. Experimental
conditions were: \( P_{\text{solar}} = 3.5 \, \text{kW} \), \( T_{\text{reduction}} = 1450 \, ^\circ \text{C} \), \( \dot{V}_{\text{Ar}} = 0.625 \, \text{L min}^{-1} \) and \( \dot{V}_{\text{CO2}} = 3 \, \text{L min}^{-1} \).

As expected, lower temperatures resulted in higher CO concentration and the highest rates were observed at \( T_{\text{start oxidation}} = 700 \, ^\circ \text{C} \) where average and peak CO\(_2\) to CO conversions were 40 % and 83 %, respectively. Comparing the conversion to previous experiments with reduction under atmospheric pressure and at the same \( T_{\text{start oxidation}} = 800 \, ^\circ \text{C} \) (Chapter 3), the average conversion was increased from 7 to 27 % and the peak conversion from 26 to 73 %. These results indicate that with the used type of reactor, vacuum operation does not only improve the reduction step (Equation 1.5) but also the conversion during oxidation (Equations 1.6 and 1.7).

Figure 4.5. Nominal reactor temperature, pressure, specific O\(_2\) rate and CO rate and concentration of cycles with varying \( T_{\text{start oxidation}} \). Experimental conditions: \( P_{\text{solar}} = 3.5 \, \text{kW} \), \( T_{\text{reduction}} = 1450 \, ^\circ \text{C} \), \( \dot{V}_{\text{Ar}} = 0.625 \, \text{L min}^{-1} \) and \( \dot{V}_{\text{CO2}} = 3 \, \text{L min}^{-1} \).

**Ambient air purging** - Experiments using a combination of inert gas purging and vacuum pumping revealed that the inert gas flow is not improving the performance and would therefore ideally be omitted (cf.
Figure 4.3. However, a controlled gas inflow to the reactor during the reduction step is required to establish a defined flow field in the reactor that prevents a natural convection flow that transports CeO$_2$(g) to the reactor front. To avoid the energy penalty associated with the inert gas production while maintaining the required flow field we substituted the argon purge with an inflow of ambient air. Air was injected only while the reactor was at vacuum pressures to avoid re-oxidation of ceria according to operation mode #3 in Figure 4.2.

**Figure 4.6** shows the nominal reactor temperature, total reactor pressure and O$_2$ and CO rates in the outlet stream of the reactor for such a cycle performed with $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1450$ °C, $V_{\text{air}} = 0.2$ L min$^{-1}$, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C, $V_{\text{CO2}} = 7$ L min$^{-1}$. Also indicated is the amount of O$_2$ that is contained in the injected air (dashed line). The O$_2$ peak (solid line) corresponds to the sum of the injected oxygen plus the O$_2$ released by ceria.

**Figure 4.6.** Nominal reactor temperature, pressure and specific O$_2$ and CO rates for a CO$_2$ splitting cycle with ambient air purging during the reduction step. The dashed line indicates the injected O$_2$ rate. Experimental conditions: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1450$ °C, $V_{\text{air}} = 0.2$ L min$^{-1}$, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C, $V_{\text{CO2}} = 7$ L min$^{-1}$. 
Note that humid ambient air without pre-treatment was used. $\eta_{\text{solar-to-fuel}}$ was similar but slightly lower compared to cycles where Ar was used with $\eta_{\text{solar-to-fuel}} = 3.83\%$ for air purging vs. $\eta_{\text{solar-to-fuel}} = 3.94\%$ with Ar as purge gas. The presented operation mode effectively protects the sensitive reactor components from CeO$_2$(g) and eliminates the need for an inert gas separation and distribution system with all its associated energy and economic penalties.

**Alternative window option** – The most critical component of the reactor in a scale-up is most probably the required quartz window that has to withstand a pressure difference of close to 1 atm. All experiments presented so far were conducted with a flat quartz disk window (see Figure 4.1 (a)). This type of window is convenient for lab-scale experiments, however it is questionable if such a window design is scalable because the required window thickness to withstand the pressure differences might become unpractical. Therefore we investigated an alternative window design for vacuum operation that features a spherical shape to minimize tensile bending stresses in the material, for which quartz is especially sensitive. The design is schematically shown in Figure 4.1 (b) and more details on the design are found in the experimental section. We experimentally tested both window options during multiple subsequent cycles at the same experimental conditions which were: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1500$ °C, $V_{\text{Ar}} = 0.625$ L min$^{-1}$, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 750$ °C, $V_{\text{CO}_2} = 7$ L min$^{-1}$. Figure 4.7 shows photographs of both window options during cold state and during operation in the HFSS. No cracking or overheating occurred and the chosen flow configurations effectively avoided back-flow to the reactor front with both window options. The reactor’s performance with both window options was similar except for a slightly higher $t_{\text{reduction}}$ with the curved window (12.9 vs. 12.1 min), presumably due to a lower total transmissivity of the curved window. Both windows are made from similar quartz glass quality and have the same thickness (4 mm). Reflection losses are expected to be approximately 0.5 % smaller at the curved window as predicted by Monte-Carlo ray tracing simulations due to lower
incident angles on the window surface. Higher transmission losses are therefore expected to result from slight surface imperfections that absorb radiation and ripples that could slightly de-focus the beam by a lens effect in the curved window. The resulting higher $Q_{\text{solar}}$ led to slightly lower $\eta_{\text{solar-to-fuel}}$ of 4.54% with the curved window compared to 4.89% with the flat window. The scalability of a similar dome window design has been assessed numerically by Mecit et al. for a 1.7 m - diameter window that was designed for $P_{\text{solar}} = 5$ MW and a pressure difference of 5 bars. \cite{130,131}

Figure 4.7. Photographs of 2 different vacuum quartz windows mounted on reactor front (left) and during operation in the HFSS (right). Top row: flat disk window; bottom row: spherical cap window.
**Purging vs. pumping** - The advantages of vacuum operation compared to inert gas purging to lower $p_{O_2}$ during thermal reduction become evident when comparing experimental results using the two operating modes at otherwise same experimental conditions. **Figure 4.8** shows the nominal solar reactor temperature, the reactor pressure and the O$_2$ and CO evolution rates during CO$_2$ splitting redox cycles obtained at atmospheric pressure (dashed lines) and at vacuum pressure (solid lines). Experimental conditions were: $P_{\text{sol}} = 3.5$ kW, $T_{\text{reduction}} = 1500$ °C, $T_{\text{start oxidation}} = 1000$ °C, $T_{\text{end oxidation}} = 600$ °C and $\dot{V}_{\text{CO}_2} = 7$ L min$^{-1}$. $\dot{V}_{\text{Ar}}$ was 7 L min$^{-1}$ and 0.625 L min$^{-1}$ during atmospheric and vacuum reduction, respectively. Operation under vacuum had two major beneficial effects on the performance of the reactor: the heating rates were higher and the fuel yield per cycle was larger. Under vacuum the average heating rate was 65 °C min$^{-1}$ compared to 56 °C min$^{-1}$ for atmospheric operation which decreased the reduction time from 16.0 min to 13.9 min. We explain this behavior by two effects. The more obvious difference was that a lower Ar flow rate was used under vacuum conditions which decreased the sensible heating load for the gas stream. However, experiments with similar flow rates under vacuum and atmospheric pressure indicated that this effect is small and not sufficient to explain the observed difference. The second difference presumably was due to different conduction heat losses to the steel shell of the reactor. At vacuum pressures the gas phase thermal conductivity is very low which lowered the effective conductivity of the insulation material that consisted of an open-porous structure, implying that its pores were also evacuated. This hypothesis was confirmed by the approximately 17 °C lower temperatures observed at the outer steel shell of the reactor when operated under vacuum compared to atmospheric pressure.

The key improvement with vacuum operation was an increased O$_2$ evolution of 5.34 L compared to 3.11 L at atmospheric operation which is explained by the one order-of-magnitude lower $p_{O_2}$ at the end of the reduction step of $4.75 \cdot 10^{-3}$ bar at vacuum vs. $4.25 \cdot 10^{-2}$ bar at
Vacuum Operation

atmospheric operation. The peak O$_2$ rates were 0.32 L min$^{-1}$ and 0.66 L min$^{-1}$ for atmospheric and vacuum operation, respectively, associated to the lower $p_{O_2}$ and the increased heating rate during vacuum operation. As an added benefit, the CO$_2$ conversion was 69% higher when conducting the reduction under vacuum compared to atmospheric pressure reduction due to the higher ceria nonstoichiometry achieved.

The energy required to decrease $p_{O_2}$ under vacuum ($Q_{Ar}+Q_{pump}$) was 100 kJ and therewith lower than under atmospheric pressure where $Q_{Ar} = 250$ kJ, despite the lower $p_{O_2}$ achieved under vacuum. This underlines that vacuum pumping is the more energy efficient method of lowering $p_{O_2}$, which is in agreement with thermodynamic calculations.$^{53, 83, 128}$

![Diagram of solar reactor temperatures, pressures, and specific O$_2$ and CO evolution rates during CO$_2$ splitting cycles performed at atmospheric pressure (dashed lines) and at vacuum pressure (solid lines) under the otherwise same experimental conditions: $P_{solar} = 3.5$ kW, $T_{red} = 1500$ °C, $T_{start oxidation} = 1000$ °C, $T_{end oxidation} = 600$ °C, $V_{CO_2} = 7$ L min$^{-1}$ and $V_{Ar} = 7$ L min$^{-1}$ and 0.625 L min$^{-1}$ during atmospheric and vacuum reduction, respectively.]

Figure 4.8. Nominal solar reactor temperatures, pressures and specific O$_2$ and CO evolution rates during CO$_2$ splitting cycles performed at atmospheric pressure (dashed lines) and at vacuum pressure (solid lines) under the otherwise same experimental conditions: $P_{solar} = 3.5$ kW, $T_{red} = 1500$ °C, $T_{start oxidation} = 1000$ °C, $T_{end oxidation} = 600$ °C, $V_{CO_2} = 7$ L min$^{-1}$ and $V_{Ar} = 7$ L min$^{-1}$ and 0.625 L min$^{-1}$ during atmospheric and vacuum reduction, respectively.
**Optimized conditions** – Combining the findings from the presented operation modes and parameter variations we performed subsequent cycles at conditions that maximize $\eta_{\text{solar-to-fuel}}$. Figure 4.9 (a) shows the temperature, pressure and O$_2$ and CO evolution rates of 5 subsequent cycles at such conditions, and in (b) cycles number 2-5 are plotted on top of each other to illustrate the reproducibility (each cycle starting at $t = 0$ min). The experimental conditions and results are listed in Table 4.1 along with an optimized cycle at atmospheric pressure for direct comparison (all values from the 3rd subsequent cycle).

The reactor featured stable performance without observable degradation. The peak and average heating rates were 139 and 81 °C min$^{-1}$, respectively, resulting in $t_{\text{reduction}} = 9.3$ min. Based on cycles #2-5, the solar-to-fuel energy conversion efficiency $\eta_{\text{solar-to-fuel}}$ was 5.25 % (standard deviation between cycles: 0.04 %). This value is more than twice as high as for optimized cycles with inert gas purging instead of vacuum pumping and, to the best of our knowledge, the highest reported value for solar-thermochemical splitting of CO$_2$.
Figure 4.9. (a) Temperature, pressure and specific O\textsubscript{2} and CO evolution rates during 5 subsequent CO\textsubscript{2} splitting reactor cycles with reduction under vacuum at optimized experimental conditions (listed in Table 4.1). (b) Cycles #2-5 plotted on top of each other (each cycle starting at $t = 0$).
Table 4.1. Solar experimental conditions and results for a CO$_2$ splitting redox cycle conducted at atmospheric pressure and at vacuum pressure during the thermal reduction step with the gen-2 reactor at the same $P_{\text{solar}}$.

<table>
<thead>
<tr>
<th>Operating pressure reduction</th>
<th>atmospheric</th>
<th>vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria RPC mass (g)</td>
<td>1728</td>
<td></td>
</tr>
<tr>
<td>Solar radiative power input, $P_{\text{solar}}$ (kW)</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Reduction temperature, $T_{\text{reduction}}$ ($^\circ$C)</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Start of oxidation temperature, $T_{\text{start oxidation}}$ ($^\circ$C)</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>CO$<em>2$ flow rate oxidation, $V</em>{\text{CO}_2}$ (L min$^{-1}$)</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>End of oxidation temperature, $T_{\text{end oxidation}}$ ($^\circ$C)</td>
<td>700 750</td>
<td></td>
</tr>
<tr>
<td>Ar flow rate reduction, $V_{\text{Ar}}$ (L min$^{-1}$)</td>
<td>7 0.625</td>
<td></td>
</tr>
<tr>
<td>Reduction pressure, $p_{\text{reduction}}$ (mbar)</td>
<td>atmospheric 11.4±1.7</td>
<td></td>
</tr>
<tr>
<td>Reduction duration, $t_{\text{reduction}}$ (min)</td>
<td>10.6 9.3</td>
<td></td>
</tr>
<tr>
<td>Cycle duration (min)</td>
<td>29.3 25.8</td>
<td></td>
</tr>
<tr>
<td>Mean heating rate (°C min$^{-1}$)</td>
<td>76 81</td>
<td></td>
</tr>
<tr>
<td>Peak heating rate (°C min$^{-1}$)</td>
<td>127 139</td>
<td></td>
</tr>
<tr>
<td>Peak specific O$_2$ evolution rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>0.30±0.03 0.56±0.01</td>
<td></td>
</tr>
<tr>
<td>Peak O$_2$ evolution rate (L min$^{-1}$)</td>
<td>0.51±0.05 0.96±0.01</td>
<td></td>
</tr>
<tr>
<td>Absolute O$_2$ evolution (L)</td>
<td>2.85±0.06 4.93±0.07</td>
<td></td>
</tr>
<tr>
<td>Peak specific CO release rate (mL min$^{-1}$ g$^{-1}$CeO$_2$)</td>
<td>0.68±0.08 1.37±0.13</td>
<td></td>
</tr>
<tr>
<td>Peak CO release rate (L min$^{-1}$)</td>
<td>1.17±0.13 2.36±0.22</td>
<td></td>
</tr>
<tr>
<td>Absolute CO release (L)</td>
<td>6.10±0.67 10.48±0.97</td>
<td></td>
</tr>
<tr>
<td>CO$_2$-to-CO conversion (%)</td>
<td>8.5 18.4</td>
<td></td>
</tr>
<tr>
<td>Molar ratio CO:O$_2$ (-)</td>
<td>2.14±0.28 2.13±0.23</td>
<td></td>
</tr>
<tr>
<td>Oxygen partial pressure $p_{O_2}$ at end of reduction (bar)</td>
<td>6.56·10$^{-2}$ 6.86·10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Argon separation energy, $Q_{\text{Ar}}$ (kJ)</td>
<td>165.6</td>
<td>14.0</td>
</tr>
<tr>
<td>Vacuum pumping energy, $Q_{\text{pump}}$ (kJ)</td>
<td>0</td>
<td>56.9</td>
</tr>
<tr>
<td>Solar-to-fuel energy conversion efficiency, $\eta_{\text{solar-to-fuel}}$ (%)</td>
<td>2.58±0.06 5.26±0.08</td>
<td></td>
</tr>
</tbody>
</table>
**Energy balance** - To better understand the thermal performance of the reactor and to identify the potential for further improvement, an energy balance based on the experimental data of the optimized cycles (Figure 4.9) was calculated. **Figure 4.10** visualizes the energy balance whereby 100% correspond to the total heat input to the process (equal to the denominator in the efficiency definition in Equation 4.1, \( Q_{\text{solar}} + Q_{\text{pump}} + Q_{\text{Ar}} \)). The underlying assumptions for the calculations are stated in Section 4.2.

Due to low \( V_{\text{Ar}} \) used during vacuum operation, only 0.3% of the energy input was required for heating of the inert gas to the reactor temperature, which indicates that gas-phase heat recovery during the reduction is not necessary at the conditions applied.

Interestingly, the energy required for vacuum pumping and Ar production was also small with fractions of 2.4% and 0.6%, respectively. The energy for vacuum pumping was low because of the moderate vacuum pressure level (~10^{-2} bar) applied in this study. However, it is important to be aware that these heat streams need to be converted to mechanical work or electricity before they can be used for vacuum pumping or inert gas separation, which increases the system complexity and cost. Note that, because \( Q_{\text{pump}} \ll Q_{\text{solar}} \), uncertainties in the assumed pump efficiency \( \eta_{\text{pump}} \) (Equation 4.5) have little influence on \( \eta_{\text{solar-to-fuel}} \). For example, assuming \( \eta_{\text{pump}} \) would be lowered by a factor of 2, \( \eta_{\text{solar-to-fuel}} \) would only decrease from 5.25% to 5.14%.

The losses by re-radiation from the reactor cavity were 8.2% and thereby smaller than values often found in literature.\(^{53, 55, 83, 128}\) The difference arises because the absorption efficiency is usually calculated assuming a constant absorber temperature at \( T_{\text{reduction}} \). In the batch-type operating mode applied in the present study, the heat is not supplied at \( T_{\text{reduction}} \) but in average at a lower temperature due to the transient temperature profile. Therefore, the re-radiation from the cavity has to be integrated over the reduction step according to Equation 4.7. As a consequence, the radiation losses were only about
50 % compared to a constant-temperature process at $T_{\text{reduction}}$. $Q_{\text{rerad}}$ could be further lowered by shortening the reduction time duration, either by decreasing the other heat losses or by increasing the solar concentration ratio.

The reaction enthalpy for the reduction of ceria amounted to 8.8 % of the total heat input. Note that this value is higher than $\eta_{\text{solar-to-fuel}}$ because a fraction of it is released as heat during the exothermic oxidation reaction (reduction enthalpy of ceria $\sim 475$ kJ per mole of atomic oxygen, heating value of CO = 283 kJ/mole). Sensible heating of ceria required about one fourth (26.4 %) of the total heat input. This fraction could only be lowered by the technically challenging recovery of the sensible heat of solid ceria, or by lowering the temperature swing between the reduction and oxidation steps.

The largest fraction of the energy input was required for heating inert reactor materials such as the insulation or was lost to water cooled parts at the reactor front. Losses to the water cooled parts could be lowered by a more advanced design of the reactor front or even avoided if an uncooled front would be implemented. Transient heating of inert reactor materials is inevitable with the used batch-type operating mode. Nevertheless, we expect that this fraction could be significantly lowered by using more advanced, low heat-capacity insulation materials.

Losses from the steel shell by convection and radiation were significant and amounted to 9.3 %, mainly because of the lab-scale size of the reactor with its inherently large surface-to-volume ratio. These losses could readily be decreased by better insulation, a low-emissivity coating of the steel shell, and by increasing the overall size of the reactor.
Active cooling – The results from the previous section indicated that sensible heating and cooling of ceria and the reactor insulation represents a main irreversibility of the process since currently all sensible heat released during cooling is lost. In an attempt to extract this heat from the reactor, it was actively cooled from $T_{\text{reduction}}$ to $T_{\text{start oxidation}}$ by flowing $N_2$ at a high flow rate through the reactor. Figure 4.11 shows the reactor temperature during a heating-cooling cycle with active cooling, the rate of heat removal, and the temperature of $N_2$ at the outlet of the reactor. For comparison, the reactor temperature of a cycle without active cooling is also indicated (dashed lines). Experimental conditions were: $P_{\text{solar}} = 3.5$ kW, $T_{\text{reduction}} = 1500$ °C, $\dot{V}_{\text{Ar}} = 7$ L min$^{-1}$ (reduction) and $\dot{V}_{N2} = 100$ L min$^{-1}$ during active cooling from 1500 °C to 1000 °C.

The peak and average heat removal rates were 2.91 and 2.67 kW, respectively, and the integrated amount of heat removed with the $N_2$ stream corresponded to 19 % of $Q_{\text{solar}}$ of an optimized cycle (cf. Figure
The temperature of the N\(_2\) stream at the reactor outlet reached a peak value of 1246 °C and then gradually decreased to 1018 °C. The active cooling with N\(_2\) shortened the cooling time duration from 8.65 min to 2.75 min. This procedure could therefore be used as a tool to actively control the cooling time duration to match the time durations of the solar with the non-solar steps. This is particularly important when considering simultaneous operation of multiple reactors for constantly using the precious concentrated solar radiation. The heat removed could be utilized for electricity generation to drive the vacuum pump and other auxiliaries. Alternatively, a second reactor could be pre-heated (solid-solid heat recovery). Also the integration to other processes could be envisioned, such as for example CO\(_2\) capture. Note that the shown cooling cycle was not optimized with respect to the flow field, pressure, or flow rates used but serves only as a preliminary demonstration of the possibility to extract useful heat from the reactor during cool-down.

**Figure 4.11.** Temperature profile, power removed, and gas outlet temperature for a heating-cooling cycle performed without active cooling (dashed lines) and active cooling from \(T_{\text{reduction}} = 1500\) °C to \(T_{\text{start oxidation}} = 1000\) °C (solid lines). Experimental conditions were: \(P_{\text{solar}} = 3.5\) kW, \(V_{N2} = 100\) L min\(^{-1}\).
4.4 Summary and Conclusions

The operation of a solar reactor for thermochemical splitting of CO$_2$ and H$_2$O via ceria redox reactions was experimentally investigated at vacuum pressures during the thermal reduction step and atmospheric pressure during the oxidation step. A direct comparison of vacuum operation to operation at atmospheric pressure with inert gas purging revealed decreased heat losses and a 73 % higher fuel yield. Simultaneous vacuum pumping and purging indicated that combinations of the two methods are not favorable and pure vacuum pumping would be desirable, however, a small inflow of gas was required to protect critical reactor components. To avoid the use of inert gas, we presented an operating mode that used ambient air instead of Ar with minimal loss in performance. A variation of the total pressure during reduction in the range 100 – 10 mbar revealed increasing efficiency at lower pressures.

During optimized cycles at $P_{\text{solar}} = 4.1$ kW, a reduction temperature of $T_{\text{reduction}} = 1500$ °C and a reduction pressure of $p_{\text{reduction}} = 10$ mbar, $\eta_{\text{solar-to-fuel}}$ for CO$_2$ splitting was 5.25 %. An energy balance calculation revealed further potential for improvement by applying low heat capacity insulation materials, further reducing $p_{\text{reduction}}$, and recovering the sensible heat of ceria. In a first step towards solid heat recovery, active cooling with nitrogen was applied after reduction and 19 % of $Q_{\text{solar}}$ were extracted from the reactor.
Chapter 5

Outlook and Research Recommendations

Substantial progress was made in the field of solar thermochemical H$_2$O and CO$_2$ splitting during the last few years. Nevertheless, further major improvements are required to render the process economically interesting. Similar to concentrated solar power plants, the main cost is expected to arise from the concentrating facility, therefore increasing the energy efficiency of the solar-to-chemical conversion step should be the main focus of future research.

The production chain to syngas includes capturing CO$_2$, concentrating solar radiation, and thermochemical splitting of H$_2$O and CO$_2$ in a solar reactor. Subsequent processing of the syngas could include H$_2$O and CO$_2$ removal, compression, FT-synthesis, and refining of the FT products.

Capture of CO$_2$ from ambient air or from flue gases of combustion processes is currently being studied also for carbon capture and storage (CCS) projects. The possibility of using process heat from other process steps as energy input (e.g. from exothermic FT-synthesis) could be considered.

The concentration of solar radiation using mirrors has already been quite well studied for concentrated solar power (CSP) applications. The currently required temperatures and thereby the solar concentration ratios for thermochemical fuel production however exceed by far those required for electricity generation. Dish concentrators could readily reach the required solar concentration ratios (>2000 suns) while central concentration systems such as
current solar tower technology offers much lower concentration ratios (typically <1500 suns), which are not sufficient to operate efficiently at the required temperatures. To make better use of scaling effects for the reactor and peripheral equipment, a central solar tower system might however be desirable. Therefore, the feasibility – and associated cost – of high concentration solar towers should be investigated, for example by using curved heliostats with variable focal lengths.

The conversion step from \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) to syngas currently causes the largest inefficiency in the process chain and therefore the focus of research should be on its further development. One of the key components dictating its performance is the redox material used. Currently the best demonstrated performance under realistic conditions of heat and mass transfer in a solar reactor was obtained using ceria. Future candidate metal oxides should ideally reduce more easily than ceria (i.e. at lower temperature), but offer similarly favorable oxidation thermodynamics with \( \text{H}_2\text{O} / \text{CO}_2 \). Rapid redox kinetics, cycling stability, abundance and low cost are further important characteristics of potential redox materials.

The structure of the material is important for efficient heat and mass transfer. While improvements have already been made, it has not yet been optimized and it is anticipated that a great potential lies in optimizing the pore morphology as the experimental results still indicated significant temperature gradients across the structure. The large scale pores (currently in the mm-range) should be tailored to ensure deeper penetration of solar radiation to achieve more uniform heating. Gradients in pore size with larger pores at the irradiated surface for low optical thickness and smaller pores towards the back side might be helpful. The engineering of the porosities can be done numerically.\(^9^9\) One possible method to manufacture tailored structures is by producing polymer foam templates by 3D printing and then applying the same replication method as used in this thesis.\(^13^2\)

The solar reactor needs to be further improved in terms of heat- and mass transfer properties and in terms of operating conditions and
strategy. An important constraint is that the reactor should remain simple, robust, scalable, and cheap. The requirement for long-term operation, ideally without maintenance, limits the possibility of using moving parts that operate at high temperature. Based on the results from this thesis, further investigations concerning the reactor and the operating conditions could include:

- Even lower total pressures during the thermal reduction step than studied in this thesis could be beneficial for efficiency. However, the feasibility on an industrial scale needs to be considered, and the energy for vacuum pumping needs to be carefully assessed to ensure that it does not become excessively large compared to the heating value of the fuel produced.

- A modified operating mode that aims at pumping the released O$_2$ at the highest (thermodynamically) possible pressure could be considered. In a cyclic operation mode with stationary redox material (as applied in this thesis) this could be achieved by heating the reactor to the reduction temperature at atmospheric pressure and only then start decreasing the pressure. This would allow to lower the theoretic pumping work compared to pumping at the minimum pressure level while heating the reactor (as it was done experimentally). A similar concept has been proposed for a particle based reactor concept with multiple reduction chambers.\textsuperscript{84} The availability of vacuum pump systems that operate efficiently under transient pressure conditions needs to be assessed. Also the stability of the RPC structure against cracks from chemical expansion during very rapid reduction has to be evaluated.

- The utilization of the sensible heat of the solids (ceria and insulation) released upon cooling needs to be assessed. It could for example be used to pre-heat another reactor (solid-solid heat recovery) or converted to electricity that is in turn used for the parasitic power requirements (e.g. vacuum pumping).
• A significant fraction of the solar energy input is currently required for heating the inert insulation. A layered design with low heat capacity insulation materials could help to lower this energy input.

• The experimental results indicate favorable efficiencies towards even higher reduction temperatures. With the present reactor concept this is not considered practical due to degradation of the monolithic material structure and the insulation. Alternative reactor concepts could be considered that might allow higher operating temperatures, such as for example using a falling film of directly irradiated particles. In such a concept, degradation of the particles by grain growth, agglomeration and sublimation might be less problematic as continuous reconditioning of the particles could be envisioned.

• The option of using ambient air as purge gas to protect the quartz window during reduction under vacuum should be further investigated. Especially, the possible formation of nitrogen oxides needs to be assessed.

The measurement of the nonstoichiometry distribution in the reactor could be further developed. A higher spatial resolution can be accomplished by monitoring the weight change during oxidation in a thermogravimeter. Possible re-oxidation in air at ambient temperature and homogenization of nonstoichiometry through oxygen bulk diffusion need to be excluded. The resulting data would be valuable to validate numerical heat and mass transfer models.

Heat recovery experiments should be further pursued with elevated N$_2$ inlet temperatures to extract the heat of the solids at a higher temperature.

Scaling-up of the reactor technology should be assessed. To evaluate how the heat and mass transfer performance scales, an existing numerical heat and mass transfer model could be applied. The
boundaries on the maximum realistic size of a single cavity might be
dictated by critical reactor components such as the quartz window for
vacuum and the RPC structure, which should be assessed numerically
and/or experimentally. Size limitations could be overcome by using
clusters of moderately sized reactor cavities.

System-scale modelling of the complete process chain is, amongst
others, useful to define refined requirements for the dissociation step.
It needs to be evaluated whether unreacted CO$_2$ is removed from the
syngas stream prior to FT-synthesis or not in order to identify the ideal
CO$_2$ conversion considering the whole system. There is a trade-off
because the solar reactor operates more energy efficiently at low CO$_2$
conversion while on the other hand, a large amount of unreacted CO$_2$
causes energy penalties for CO$_2$ removal (if applied), or compression
of the syngas. The system model could then also be used to study heat
integration between the various process steps. As an example, the heat
released by the exothermic FT synthesis could be used to produce
steam for the solar reactor. Furthermore, methods to deal with the
intermittency of the syngas stream must be found. Scenarios could
include storage of syngas for continuous FT-synthesis, thermal storage
for continuous syngas production, or daily start-up and shut-down of
the FT plant.

The system scale model could then also be used to conduct an
economic analysis which would help to further evaluate the potential
of the technology, and to define required target efficiencies for the
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<tr>
<td>2013-2016</td>
<td>Doctoral studies (Ph.D.), Professorship of Renewable Energy Carriers, Institute of Energy Technology, Department of Mechanical and Process Engineering, ETH Zurich, Switzerland. Supervisor: Prof. Dr. Aldo Steinfeld</td>
</tr>
<tr>
<td>2013-2016</td>
<td>Research and teaching assistant, Department of Mechanical and Process Engineering, ETH Zurich, Switzerland</td>
</tr>
<tr>
<td>2012-2013</td>
<td>Master studies (M.Sc.), ETH Zurich, Switzerland.</td>
</tr>
<tr>
<td>2011-2012</td>
<td>Industrial internship (6 months), Robert Bosch GmbH, Stuttgart, Germany</td>
</tr>
<tr>
<td>2007-2011</td>
<td>Bachelor studies (B.A.Sc.), ETH Zurich, Switzerland</td>
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<tr>
<td>2007</td>
<td>Matura, Liechtensteinisches Gymnasium Vaduz, Vaduz, Liechtenstein</td>
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</tbody>
</table>

Name       Daniel Arnold Marxer  
Nationality Liechtenstein  
Date of birth 08.08.1988
List of Publications

Journal articles


*in preparation*: Marxer, D.; Furler, P.; Takacs, M.; Steinfeld, A. Solar thermochemical splitting of CO$_2$ into separate streams of CO and O$_2$ with high selectivity, stability, conversion, and efficiency.


Conference Presentations (oral)
