

Solar Thermochemical Splitting of CO₂ in a Modular Solar Dish-Reactor System

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Abstract

We report on the experimental demonstration of a modular solar dish-reactor system to perform the splitting of CO₂ into separate streams of CO and O₂ via a 2-step thermochemical cycle based on ceria redox reaction. Since only the reduction step requires a solar input, the system comprises two solar reactors mounted side-by-side on a sun-tracking dish concentrator coupled to a secondary rotating reflector that allows for simultaneous operation of both reactors by alternating the concentrated solar input between them. Each solar reactor consists of a cavity-receiver containing a reticulated porous structure made of ceria exposed to a solar radiative power input of 6 kW at 2360 suns entering through the cavity's aperture. Process stability and system robustness are demonstrated by performing fully automated consecutive redox cycles.

Keywords: solar, fuel, concentrator, reactor, thermochemical, redox, cycle, ceria, CO₂.

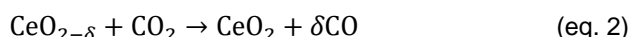
1. Introduction

This paper describes the solar technology for performing the splitting of CO₂ into separate streams of CO and O₂ via a reduction-oxidation (redox) thermochemical cycle driven by concentrated solar energy (Romero and Steinfeld, 2012, and literature cited therein). The ceria-based thermochemical redox cycle comprises two steps involving a temperature/pressure swing cyclic process:

1) the endothermic reduction of ceria, typically performed at a temperature above 1400 °C and a pressure below 0.1 bar:



2) the exothermic oxidation of reduced ceria with CO₂, typically performed at a temperature below 1000 °C and a pressure above 1 bar:



where the nonstoichiometry δ indicates the reduction extent. The net reaction is CO₂ = CO + 1/2 O₂, with fuel CO and O₂ derived in different steps and thus eliminating the need for high-temperature gas separation.

2. System Description

The solar technology for effecting the CO₂-splitting thermochemical cycle consists of a modular solar dish-reactor system with two major coupled components: the solar concentrator and the solar reactor.

2.1 The Solar Concentrator

Fig. 2.1 a) shows a schematic of the solar concentrator comprising a primary sun-tracking 4.4 m-dia., 2.2 m-focal length, parabolic reflector and a secondary rotating 1.71 m²-area 24°-tilt flat reflector (Dähler et al., 2018). This optical configuration allows to rotate the concentrator focal point among 4 positions, as depicted in Fig. 2.1 b): the two solar reactors, a water-calorimeter for solar radiative power measurements and a Lambertian target for solar flux distribution measurements. This arrangement enables the operation of the two solar reactors side-by-side for performing both redox reactions simultaneously by alternating the solar radiative input between them while making continuous and uninterrupted use of the incoming concentrated sunlight. For a normalized DNI of 1 kWm⁻², the

concentrating setup delivers a solar radiative power of up to 7680 W to the 30-mm radius aperture of the solar reactor with a mean and peak solar concentration ratio of 2710 suns and 5010 suns, respectively, yielding an overall optical efficiency of 59.6%. Detailed optical analyses based on experimentally measured and numerically simulated data identify feasible measures to increase this optical efficiency to 82% (Dähler et al., 2018).

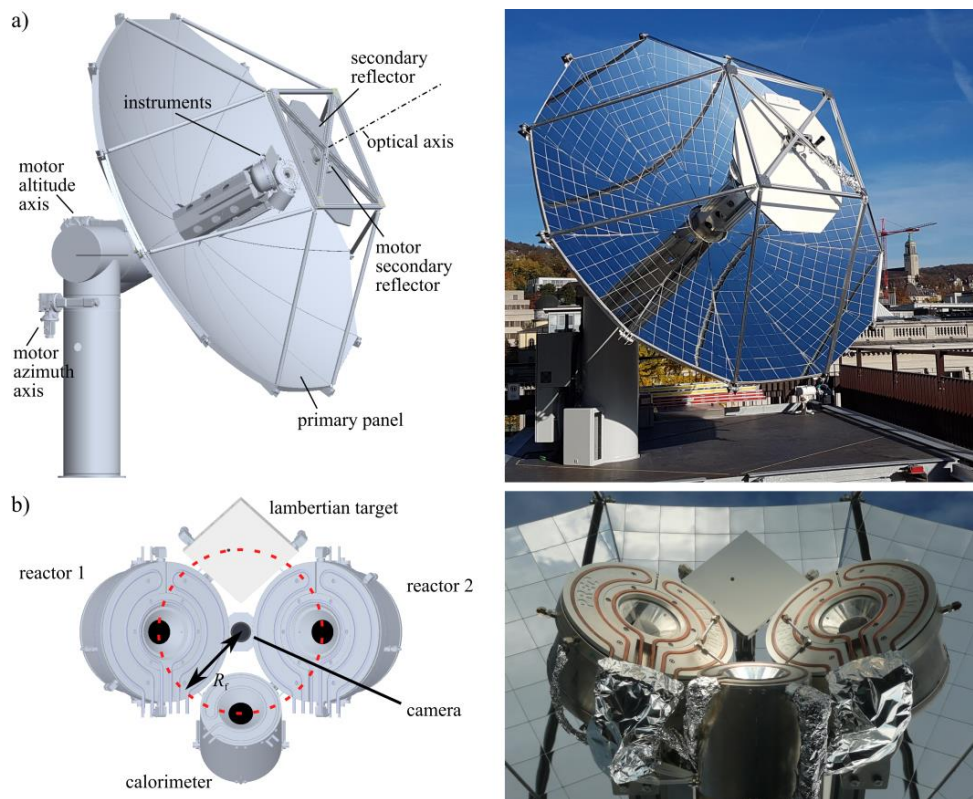


Fig. 2.1: Schematics and photographs of the solar dish system: a) 3D rendering of the primary two-axis sun-tracking parabolic dish and secondary rotating flat reflector (Dähler et al. 2018); b) solar reactors, water-calorimeter, and Lambertian target. Dashed circle indicates the focal point trajectory during rotation of the secondary reflector (reproduced from Dähler et al. 2018).

2.2 The Solar Reactor

The design and fabrication of the solar reactor has been previously described (Marxer et al., 2017); only the main features are highlighted here. It consists of a 200 mm-i.dia., 100 mm-length cylindrical cavity-receiver with a 60 mm-dia. circular aperture sealed by a 6 mm-thick clear fused quartz disk window for the access of concentrated solar radiation. The cavity contains an octagonal 35 mm-thick reticulated porous ceramic (RPC) foam-type structure made of pure ceria that is directly exposed to the solar irradiation, enabling volumetric absorption and uniform heating. The RPC structures with dual-scale porosity – mm-size pores for enhanced volumetric absorption during the reduction step and μm -size pores within the struts for enhanced mass transfer during the oxidation step – were fabricated according to the replication method (Furler et al., 2014). Two identical solar reactors were fabricated and mounted side-by-side at the focal plane of the solar concentrator (Fig. 2.1 a and b).

2.3 Measurement Instrumentation

Temperatures were measured using multiple B- and K-type thermocouples. Gas flow rates were regulated and measured using Bronkhorst electronic mass flow controllers and meters. The reactor pressures were measured using THERMOVAC TTR 101N pressure sensors. A multistage roots dry vacuum pump (Adixen ACP 28CV) in combination with multiple valves was used to evacuate the reactors during reduction. Product gas composition was analyzed on-line downstream of the solar reactors by gas chromatography (Agilent Technologies) and Siemens Ultramat 23 and Calomat 6 gas analysis units (electrochemical sensors for O_2 , IR detectors for CO and CO_2 , thermal conductivity based detectors for H_2). The direct normal irradiation (DNI) was measured with a sun-tracking pyrheliometer. The entire solar dish-reactor system is controlled by a LabView program for performing fully automated consecutive redox cycles over the whole day.

3. Results and Discussion

Fig. 3.1 shows a representative CO₂-splitting redox cycle. Plotted as a function of time are the temperature at the outer perimeter of the RPC (green), reactor pressure (red) and gas evolution of O₂ released during solar reduction (black) and CO produced during oxidation (blue). During the reduction step (eq. 1), the solar reactor was heated with concentrated sunlight to 1400 °C (measured at the outer perimeter of the RPC) while the total pressure was lowered to 4 mbar by the vacuum pump with a flow of 1 l min⁻¹ Ar as sweep gas. The oxidation step (eq. 2) was initiated once the reactor cooled down to 1000 °C by providing a CO₂ flow of 7 l min⁻¹ that reacted with the reduced ceria to form CO.

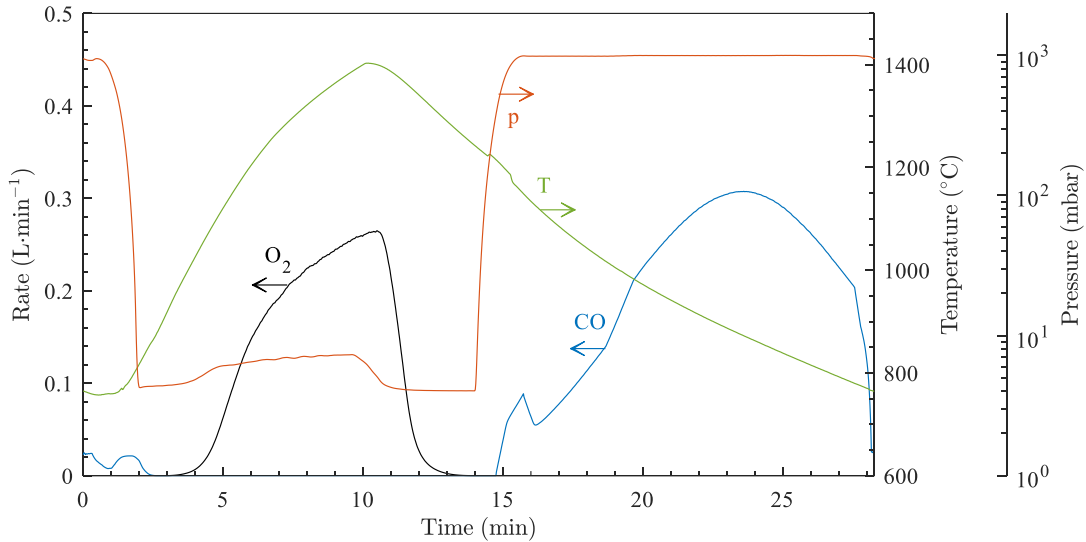


Fig. 3.1: Measured RPC temperature, reactor pressure and gas evolution rates for a representative CO₂-splitting redox cycle.

Fig. 3.2 shows a representative on-sun run with fully-automated 32 consecutive CO₂-splitting cycles as described above. Plotted as function of time are the measured DNI (yellow line) over the day, mean RPC temperatures of both solar reactors (solid lines), and integrated specific gas production per cycle (O₂: hollow circles, CO: asterisks) for both solar reactors operated in alternate mode – one reactor is performing the solar reduction step (eq. 1) while the other reactor is performing the oxidation step (eq. 2). The ceria mass loading of each solar reactor was 3752 g and 3760 g. The solar power input and mean solar flux concentration through the aperture, measured between the cycles (white areas in Fig. 3.2), were up to 5.9 kW and 2360 suns, respectively. Averaged over these cycles, the peak and total O₂ evolution was 0.29 ml g⁻¹CeO₂ min⁻¹ and 1.44 ml g⁻¹CeO₂, respectively, and the peak and total CO production was 0.31 ml g⁻¹CeO₂ min⁻¹ and 2.89 ml g⁻¹CeO₂, respectively. Peak CO₂-to-CO molar conversions of 83% and $\eta_{\text{solar-to-fuel}}$ of 5.25% (without heat recovery) were previously demonstrated (Marxer et al., 2017).

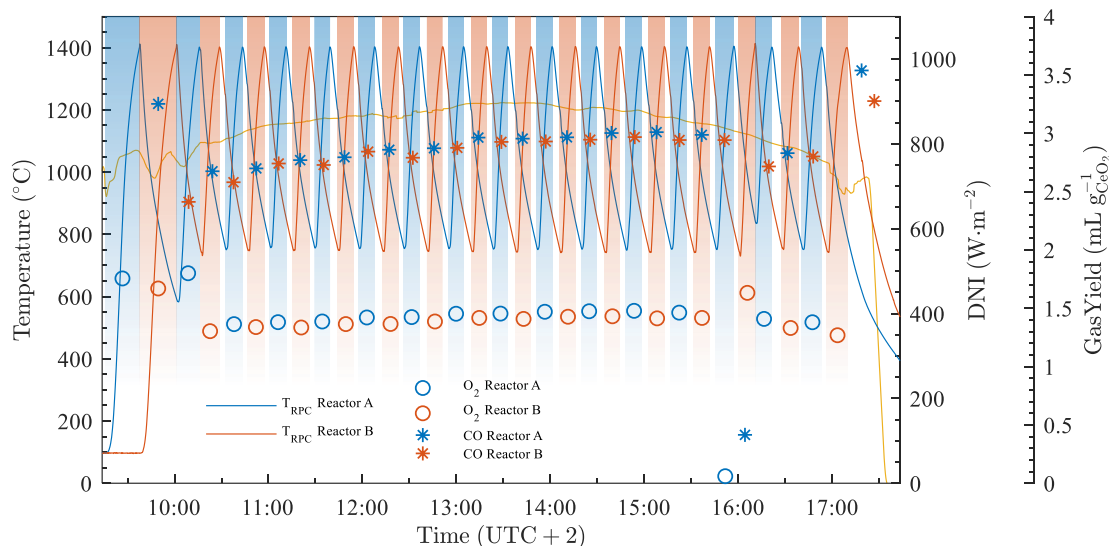


Fig. 3.2: Measured RPC temperatures, DNI, and CO and O₂ specific gas yield per cycle over 32 consecutive CO₂-splitting cycles of both solar reactors A and B operated in alternate mode: while reactor A is performing the solar reduction step (eq. 1), reactor B is performing the oxidation step (eq. 2) and vice versa.

4. Summary and Conclusions

A modular solar dish-reactor system was developed for the production of solar CO from CO₂ via a ceria-based thermochemical redox cycle using concentrated solar energy. Multiple consecutive CO₂ splitting cycles were demonstrated during fully-automated on-sun daily runs. These solar runs demonstrate the stability and robustness of the system and advance the technological readiness and its industrial implementation. Future development work will be aimed at demonstrating the solar reactor technology for splitting H₂O into separate streams of H₂ and O₂, and thus produce syngas for the synthesis of liquid hydrocarbon fuels.

5. Acknowledgments

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