

Pilot-scale solar reactor operation and characterization for fuel production via the Zn/ZnO thermochemical cycle



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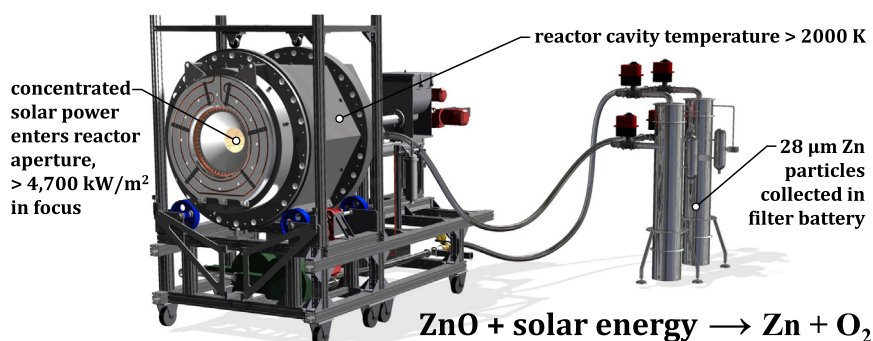
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HIGHLIGHTS

- First ever successful demonstration of a 100 kW_{th} scale reactor for ZnO dissociation.
- Nearly 100 h of high temperature solar reactor operation.
- Achieved reactor solar-to-chemical efficiency of 3%.
- Over 28 kg of ZnO dissociation, with a maximum dissociate rate of 28 g/min.
- Record level sustained reaction temperatures above 2000 K and solar flux above 4000 kW/m².

GRAPHICAL ABSTRACT



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ABSTRACT

Successful demonstration and promising characterization of a solar reactor pilot plant for thermal reduction of ZnO as part of a two-step water and CO₂ splitting cycle has been accomplished at the 100 kW_{th} scale in a 1 MW solar furnace. The solar reactor pilot plant was operated for over 97 h and achieved sustained reaction temperatures well above 2000 K, while demonstrating ZnO dissociation rates as high as 28 g/min totaling over 28 kg of processed reactant during 13 full days of experimentation. In-situ, high temperature, flow visualization of the quartz window enabled the unimpeded operation of the solar reactor. As many as three consecutive full day experiments were conducted without complication. Solar power delivered to the reaction cavity ranged between 90 and 128 kW_{th}, at peak solar concentrations as high as 4671 kW/m². The products Zn and O₂ were quenched with Ar(g) and recovered in a filter battery, where collected particles contained molar Zn-content as high as 44%. During experimentation, switching between product collection filter cartridges resulted in 54 unique experiments, where a maximum solar-to-chemical efficiency of 3% was recorded for the solar reactor. Robust characterization of the product quenching device revealed inherent limitations in its effectiveness, and thus solar-to-fuel energy conversion efficiency was limited to 0.24% if it would have been possible to supply 4640 L_n/min of Ar(g). Further, only a limitation on available experimental time prohibited the demonstration of significantly higher dissociation rates, achievable with higher ZnO reactant feed rates. While the use of large volumes of quenching Ar(g) to separate the reaction products remains a significant obstacle to achieving higher solar-to-fuel efficiencies, demonstration of solar reactor technology at the pilot-scale represents significant progress toward the realization of industrial-scale solar fuels production.

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Nomenclature

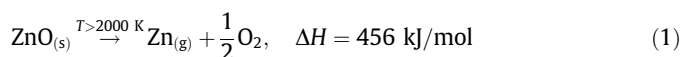
a_{BET}	BET specific surface area, m^2/g	p_{O_2}	partial pressure of oxygen exiting the reactor, kPa
c_i	linear regression coefficients, for i [0,3], mixed	p_{Zn}	partial pressure of Zn exiting the reactor, kPa
d_{mean}	mean particle diameter, μm	Q_{solar}	solar power input, kW
d_p	pore diameter, nm	T_{R}	reaction temperature, measured by TC-4, K
d_{sp}	spot diameter on quartz window, cm	\dot{V}_{Ar}	mass flow rate of quenching argon, $\text{L}_\text{n}/\text{min}$
HHV_{syngas}	higher heating value of syngas, kJ/mol	V_p	pore volume, cm^3/g
\dot{m}_{diss}	ZnO dissociation rate, g/min	W_{Ar}	energy penalty for argon consumption, kJ
\dot{m}_{feed}	ZnO reactant feed rate, kg/h	X_{Zn}	zinc yield, %
$n_{\text{Ar,tot}}$	moles of argon passing through the quench device, mol	ΔH	reaction enthalpy, kJ/mol
n_{O_2}	moles of oxygen exiting the reactor, mol	η_{ave}	non-specific average energy conversion efficiency, %
n_{tot}	moles of total product, mol	η_{max}	non-specific maximum energy conversion efficiency, %
n_{Zn}	moles of Zn, mol	$\eta_{\text{solar-to-chemical}}$	solar-to-chemical energy conversion efficiency, %
$n_{\text{ZnO,diss}}$	moles of ZnO dissociated, mol	$\eta_{\text{solar-to-fuel}}$	solar-to-fuel energy conversion efficiency, %
n_{ZnO}	moles of ZnO, reoxidized, mol	ρ_{bulk}	bulk density, g/cm^3
\dot{n}_{Ar}	molar flow rate of argon, mol/s	DNI	direct normal irradiance, W/m^2
\dot{n}_{O_2}	molar flow rate of oxygen, mol/s	PID	proportional–integral–derivative control, –
\dot{n}_{Zn}	molar flow rate of zinc, mol/s	PSI	Paul Scherrer Institute, –
p_0	atmospheric pressure, kPa		

1. Introduction

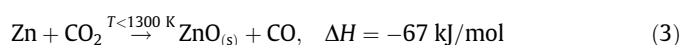
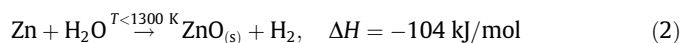
Water and CO_2 splitting thermochemical cycles driven by solar energy are being considered as a sustainable and environmentally friendly path to large scale fuel production [1–4]. Metal oxides are a promising class of materials for thermochemical cycling, for example tin, iron and zinc oxide [5–7]. For the Zn/ZnO thermochemical cycle, after high temperature thermal reduction of ZnO into metallic Zn (Eq. (1)), the Zn product is further processed via exothermic H_2O and/or CO_2 splitting reactions (Eqs. (2) and (3)), where hydrogen and/or syngas is produced and ZnO can be returned to the solar reactor to close the cycle [8]. The product gases hydrogen and/or syngas can be burned directly for power generation or used in a fuel cell [9,10]; alternatively, Fischer–Tropsch synthesis can be utilized to produce synthetic liquid hydrocarbon fuels from CO and H_2 , thus solar fuel is created with sunlight, water and carbon dioxide. The prospect of a solar-driven hydrogen energy economy has been under consideration for over 40 years [11,12], as well as the proposition that the specific redox pair Zn/ZnO could be utilized to split water using concentrated solar power [13]. Here, we continue with the Zn/ZnO thermochemical cycle that was first proposed in 1977 and experimentally demonstrated on the 2 kW laboratory-furnace scale, but at the 100 kW pilot plant scale, representing the culmination of decades of research and development into solar reactor technology, bridging the gap between research, development, and implementation.

The first step of the Zn/ZnO thermochemical cycle proceeds at temperatures above 2000 K according to Eq. (1), and the second step according to Eqs. (2) and (3), where the reaction enthalpy changes listed are referenced from standard state:

1st step: solar-driven endothermic reduction of ZnO:



2nd step: exothermic oxidation of Zn into ZnO and product gases:



Considering the utilization of captured [14] and/or point-source sequestered [15,16] carbon dioxide as the oxidizing agent in Eq. (3), the proposed production of solar fuels is carbon neutral. The Zn/ZnO thermochemical cycle possesses a uniquely high potential for solar-to-fuel energy conversion efficiency compared to other redox materials [17–20] being considered for two-step cycling. Solar-to-fuel energy conversion efficiency is defined as the ratio of the heating value of the fuel produced to the solar energy input, and based on thermodynamic considerations can be as high as 61% with heat recovery for the Zn/ZnO cycle, and 37% without heat recovery [21]. Experimental results from materials science and reactor development efforts have demonstrated that issues related to attenuation of the reactor window transmittance [22–24], separation of the products Zn and O_2 in Eq. (1) [25–27], and kinetic limitations [28–30] make achieving efficiencies close to the theoretical limit very challenging [31]. Regarding product separation, the current strategy, which utilizes large volumes of room-temperature inert gas in a quenching device, seems energetically and economically prohibitive [32,33]. Because of such difficulties, state-of-the-art water and CO_2 splitting research has shifted away from volatile metal oxide reactants and toward the partial reduction of non-volatile materials such as non-stoichiometric ceria [34–36] and perovskite materials [37]. Additionally, utilization of a carbon reducing agent such as beech charcoal [38–40] or natural gas [41] can be an effective way of overcoming product recombination and achieving high reactant conversion at lower temperature. A slip-stream of natural gas, for example, could play a significant role in synthetic fuel production while still decreasing carbon intensity significantly. Vacuum reduction of volatile redox materials is also a promising pathway to overcoming recombination difficulties, and is an active area of research and development [42,43].

Despite the shift away from volatile reactants, solar reactor technology for thermal reduction of such redox materials has been the focus of research and development efforts for over twenty years, and significant progress has been made [44,45]. Reactor concepts have spanned design strategies from packed beds [30,46,47], to aerosolized and entrained flows [38,48,49], to rotary quasi-batch arrangements [50–54]. Experimental and design progress, as well as progress in modeling efforts [55–57], has been substantial. Recently, the Paul Scherrer Institute (PSI), in collaboration with ETH Zurich, brought design, development and demonstration

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