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Solar carbothermal reduction of aerosolized ZnO particles under vacuum: Modeling, experimentation, and characterization of a drop-tube reactor

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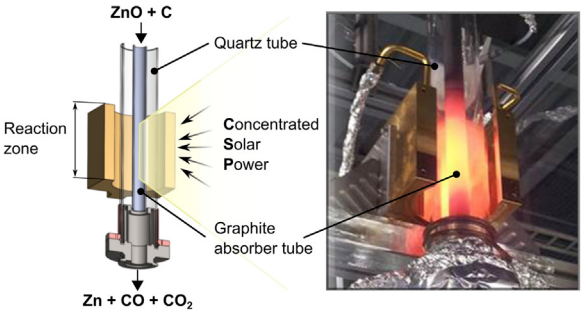
HIGHLIGHTS

- Solar vacuum drop-tube reactor extensively characterized at 1, 100 and 960 mbar.
- Zinc production is higher at 100 mbar compared to ambient pressure.
- Reactor model featuring radiative heat transfer with Monte Carlo ray tracing.
- Reaction at 1 mbar is inhibited due to insufficient particle residence time.
- Maximum zinc production predicted to be 52 mmol·min^{-1}, at a feed rate of 68 g·min^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

A vacuum aerosol particle reactor was tested for the carbothermal reduction of zinc oxide using concentrated solar power as a heat source. A steady state reactor model was developed to investigate the effect of pressure dependent particle residence time and radiative input power on the zinc production rate. Radiative heat transfer to the particle cloud is solved by Monte Carlo ray tracing, accounting for spectral and directional optical properties and temperature dependent chemical kinetics. Experiments with the solar drop-tube reactor were conducted to ascertain the reaction capacity of the system at pressures between 1 and 960 mbar by varying the reactant feed rate between 4 and 56 g·min^{-1}. Experiments show that the zinc production rate is maximal at around 100 mbar and significantly diminishes under high vacuum. Model and experimental results indicate that the reaction at 1 mbar is inhibited due to insufficient residence time and heat up of the particles in the reaction zone. Maximum experimental zinc production rate was 51.4 mmol·min^{-1} while feeding 56 g·min^{-1} of solid reactants and operating the reactor at 100 mbar with 9.8 kW of radiative input power. Extrapolation to higher feed rates with the reactor model predicts a peak zinc production capacity of 52.1 mmol·min^{-1} at a feed rate of 68 g·min^{-1}, achieving a net thermal efficiency of 3.2%.

1. Introduction

Solar-driven carbothermal reduction of ZnO to Zn is an interesting pathway to convert and store solar energy for use in Zn-air batteries, or to produce syngas via H_2O and CO_2 splitting cycles [1,2]. Syngas, a gas mixture of H_2 and CO, can be further used as a precursor to conventional liquid fuels production via Fischer-Tropsch synthesis [3]. The overall chemical reaction that describes the reduction of zinc oxide with carbon is,

$$ZnO(s) + C(s) \rightarrow Zn(g) + CO, \Delta H_{R,1400K} = 352.5\ kJ \cdot mol^{-1} \quad (1)$$

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Nomenclature

a_λ	Absorption coefficient [m^{-1}]
a_P	Planck mean absorption coefficient [m^{-1}]
A_t	Inner wall surface of discretized tube segment [m^2]
c_p	Specific heat [$J{\cdot}mol^{-1}{\cdot}K^{-1}$]
d_p	Particle diameter [μm]
$d_{10,50,90}$	Diameter on cumulative particle size distribution [μm]
E_A	Apparent activation energy [$kJ{\cdot}mol^{-1}$]
f_v	Particle phase volume fraction [–]
g	Standard gravity [$m{\cdot}s^{-2}$]
ΔH_{rxn}	Reaction enthalpy [$kJ{\cdot}mol^{-1}$]
$I_\lambda(r,\hat{s})$	Intensity of emitted radiation [$W{\cdot}m^2$]
$k_{w,p,f}$	Thermal conductivity [$W{\cdot}m^{-1}{\cdot}K^{-1}$], w = wall, p = particle, f = fluid
k_0	Arrhenius pre-exponential factor [$mol{\cdot}s^{-1}{\cdot}m^{-2}{\cdot}Pa^{-1}$; $mol{\cdot}s^{-1}{\cdot}g^{-1}{\cdot}Pa^{-1}$]
$\dot{m}$	Reactant feed rate [$g{\cdot}min^{-1}$]
n_i	Species amount [mol], i = ZnO, CO, CO_2, Zn, C
N_p	Number of particles [–]
N_{rays}	Number of rays in MC ray tracing simulation [–]
N_{seg}	Number of discretized tube segments [–]
p	Pressure [mbar or Pa]
$p_{CO,CO2}$	Partial pressure of CO and CO_2 [Pa]
P_{Pump}	Vacuum pump power [kW]
Q_{abs}	Absorbed power by particle phase [W]
$Q_{a\lambda}$	Mie theory absorption efficiency factor [–]
$Q_{s\lambda}$	Mie theory scattering efficiency factor [–]
Q_{ext}	External heat source of radiation emitted by tube [W]
Q_{int}	Internal heat source of radiation emitted by tube [W]
Q_{net}	Net incident radiative power on graphite tube [kW]
Q_{rad}	Incident radiative solar power through reflector aperture [kW]
Q_{ray}	Radiative power assigned to a single ray [W]
q_{rad}	Incident radiative flux across reflector aperture [$kW{\cdot}m^{-2}$]
∇q_r	Divergence of radiative flux [$W{\cdot}m^{-3}$]
q_z	Circumferentially averaged axial radiative power distribution [kW]
q_φ	Axial averaged angular power distribution [kW]
r	Reaction rate [$mol{\cdot}s^{-1}$], tube radius [mm]
R	Gas constant [$J{\cdot}mol^{-1}{\cdot}K^{-1}$]
$\Re_i$	Random number
s_λ	Scattering coefficient [m^{-1}]
s_{ext}	Extinction length [mm]
$\hat{s}$	Ray direction vector [–]
$S_\lambda(r,\hat{s})$	Source function [$W{\cdot}m^{-2}$]
t	Time [s]
Δt_f	Particle feed time interval [min]
T_C	C-type thermocouple temperature [K]
T_{Pyro}	Pyrometer temperature [K]
T_p	Particle phase temperature [K]
T_w	Tube wall temperature [K]
V_t	Volume of tube segment [m^3]
v_r	Average particle phase velocity [$m{\cdot}s^{-1}$]
X	ZnO conversion [%]
$z*$	Normalized axial tube coordinate [–]

Acronyms

C1	Carbon source 1, Sigma Aldrich Supelco 31616
C2	Carbon source 2, Cabot Corp Norit CA1
ETH	Swiss Federal Institute of Technology
GC	Gas Chromatograph
HFSS	High flux solar simulator
MC	Monte Carlo
PSI	Paul Scherrer Institute

Greek symbols

ς	Mie scattering theory size parameter [–], thermocouple axial position [mm]
λ	Wavelength [μm]
λ_{ray}	Wavelength assigned to ray in MC simulation [μm]
β_λ	Extinction coefficient [m^{-1}]
ρ_p	Molar particle density [$mol{\cdot}m^{-3}$]
σ	Stefan-Boltzmann constant [$W{\cdot}m^{-2}{\cdot}K^{-4}$]
$\varphi*$	Normalized circumferential tube coordinate [–]
Φ	Scattering phase function
θ	Ray scattering angle
ψ	Random ray arc angle
ω_λ	Scattering albedo [–]
Π	Equivalent zinc production rate [$mmol{\cdot}min^{-1}$]
η_{th}	Thermal efficiency [%]
τ_r	Particle residence time in reaction zone [s]

where reaction heat is provided by concentrated solar radiation to reduce ZnO at temperatures greater than 1400 K. The primary reaction route proceeds through two gas-solid reactions in which solid ZnO is first reduced by CO (Eq. (2)) to gaseous Zn, and subsequently the produced CO_2 is reduced by carbon following the Boudouard reaction (Eq. (3)) [4,5],

$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2 \quad (2)$$

$$C(s) + CO_2(g) \rightarrow 2CO \quad (3)$$

Carbon acts indirectly as a reducing agent, allowing for the reduction of ZnO at a lower temperature and with diminished recombination of the products oxygen and zinc vapor, which is a significant obstacle when operating a purely thermal ZnO dissociation cycle [6]. If carbon is supplied from carbonaceous waste process streams or from sustainable biomass sources, the production of Zn can be five times less carbon intensive using the solar-assisted pathway compared to conventional fossil-fuel-driven electrolytic or Imperial Smelting processes [7,8]. The thermodynamics of the reaction can be positively influenced by operation under vacuum [9–11], or by using inert gas for dilution, both of which result in a reduced operating temperature [5,12,13]. Vacuum operation has the advantage of improved reaction kinetics [14,15], and lower amounts of inert gas $\dot{n}$ that are necessary to maintain a certain volumetric flow rate $\dot{V}$ at reduced pressure conditions ($p_1\dot{V}_1/p_2\dot{V}_2 = \dot{n}_1/\dot{n}_2$). Thus, operation under vacuum could lead to a significant reduction in the required amount of inert gas for the process and in some cases outweigh the pumping energy penalty incurred [16].

The solar reduction of metal oxides can be performed with reactors that feature direct irradiation [13,17–20] and indirect irradiation [8,12,15,21] of the reactants. With batch or semi-batch reactors operating with a vacuum step, frequent evacuation and purging is required. Alternatively, a drop-tube reactor concept, featuring vertical orientation and continuous reactant feeding within a vacuum tube can be used [22,23]. In such a concept the drop-tube is irradiated on the outside surface, resulting in indirect radiation heat transfer to the falling reactant particles. Ideally, the reactants are dispersed into a fine particle cloud and act as a volumetric absorber with quick heat up times and fast reaction kinetics [24,25]. The main advantages of a drop-tube reactor are its inherent scalability and modularity, the low thermal inertia and robust-