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Modeling of a tubular solar reactor for continuous reduction of CeO_2: The effect of particle size and loading on radiative heat transfer and conversion

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HIGHLIGHTS

- The continuous reduction of CeO_2 particles is modeled in a solar tubular reactor.
- The effect of particle size and particle loading are studied within the reactor.
- The model couples the radiation, mass and heat transfer equations.
- Increasing particle size changes the radiative transfer, favoring CeO_2 reduction.
- CeO_2 particle loading at the reactor inlet should be kept close to 100 mg l^{-1}.

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ABSTRACT

A solar multi-tubular reactor for non-stoichiometric reduction of CeO_2 is modeled under continuous operation. An aerosol, consisting on CeO_2 particles and Argon, flows upwards through the reactor vertical tubes. Heat, mass and radiation transfer phenomena are efficiently implemented in an axisymmetric domain by using multi-mesh, multi-step, Finite-Volume and Monte Carlo methods. Reaction, particle diffusion, conduction, forced convection as well as radiation absorption, emission and anisotropic scattering are considered. The kinetic model for the non-stoichiometric reduction of CeO_2 is taken from Ishida et al. (2014). Model results at steady-state focus on the effect of changing particle loading and diameter at different average residence times. For particle diameters of 1–20 μm, increasing particle size favors uniform radiation absorption, minimizing temperature gradients. Finally, for an outer tube surface temperature of 2500 K, a particle loading of 0.1 kg/m^3 and average residence time of 30–60 s are recommended.

1. Introduction

High temperature solar processes represent an environmentally-friendly alternative to carry out material transformations for the chemical industry such as calcium carbonate calcination for solar production of lime or cement, or production of activated charcoal. Among the many applications suitable of solar thermal technologies, solar fuel production stands out. The urging need to replace fossil fuels constantly stimulates the development of renewable energy technologies and high temperature solar thermal processes are not the exception. In the last decades solar thermochemical production of Hydrogen, syngas and C2 hydrocarbons has been gaining momentum (Abanades and Flamant, 2005, 2006a, 2006b; Abanades et al., 2006; Steinfeld, 2005; Kodama, 2003; Steinfeld and Palumbo, 2001; Perkins and Weimer, 2009).

Due to its abundance, low value and the absence of CO_2 emissions, water splitting represents an interesting approach to store energy. Despite the advantages, efficient water splitting using solar energy is still an open challenge. For instance, water thermolysis requires temperatures above 2500 K to accomplish a reasonable degree of dissociation (Dincer and Acar, 2015). At this temperature, usage of a semi-permeable membrane is required to favor H_2 formation. Existing membranes require temperatures below 2500 K, so that conversion rates are still quite low due to material related limitations (Baykara, 2004). The so-called redox pair cycles for water splitting (Ambriz et al., 1982; Sibieude et al., 1982; Agrafiotis et al., 2007; Charvin et al., 2008) bypass the highly unfavoured thermolysis reaction allowing solar reactors to operate efficiently at lower temperatures.

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Among the challenges being faced by solar thermochemical technologies, design and operation of solar reactors with higher exergetic efficiencies is crucial (Agrafiotis et al., 2007). Efficiently designing a solar reactor requires accounting for highly interdependent radiation, heat, momentum and mass transfer phenomena. Additionally the materials and construction method should be resilient to thermal shocks and durable at temperatures well above 1200 K. Interest in solar reactors dates back to the 1960s and since then an ample range of designs and materials has been proposed (Funk and Reinstrom, 1964, 1966; Funk, 2001; Ambriz and Romero-Paredes, 1985; Beghi, 1986).

Relatively few studies can be found in the literature dealing with solar reactor modeling and simulation (Abanades et al., 2007; Agrafiotis et al., 2007; Palumbo et al., 2004; Petrasch and Steinfeld, 2007; Kogan et al., 2007; Valdés-Parada et al., 2011) and even fewer dealing with reactor optimization (Ozalp et al., 2015; Valades-Pelayo et al., 2015; Tescari et al., 2010; Melchior and Steinfeld, 2008). Due to the different physical phenomena that must be incorporated, simulation and optimization of solar reactors is an involved endeavor, further complicated by the existing diversity of configurations available. In this regard, solar reactors are generally classified based on the (i) metal oxide state (suspended or supported), (ii) solar heating approach (direct or indirect) and (iii) operating mode (continuous, semi-batch or batch).

The reactors most extensively studied in recent years consider direct irradiation of suspended metal oxide particles under continuous operation. This is the case given that, in principle, fluidized particles directly exposed to a concentrated radiative flux provide the most efficient means to heat a metal oxide using solar energy (Muller and Flamant, 1988; Müller and Steinfeld, 2007; Müller et al., 2003). In practice, however, difficulties arise as particle abrasion promotes dust deposition, leading to window breakage due to hotspot formation.

Several strategies to minimize this issue are found in the literature, such as using a screen flow under the window (Kogan et al., 2007) or considering a rotary cavity, so that centrifugal forces keep the particles from adhering to the window (Steinfeld, 2005; Kogan and Kogan, 2002). An alternative consists on using a supported metal oxide, allowing direct irradiation of the metal oxide without any risk of window breakage, but compromising the ability to operate the reactor continuously. Elaborate designs for supported metal oxides have been devised to circumvent this limitation, such as dual rotating (Roeb et al., 2011; Kaneko et al., 2007) or concentric counter-rotating reactors (Diver et al., 2010). These configurations allow quasi-continuous operation by alternating reduction and oxidation; however, alternating stages ultimately leads to high sensible heat losses and low thermal-to-fuel efficiencies ranging 2% (Furler et al., 2012).

Another possibility consists on resorting to indirectly irradiated solar reactors. This configuration does not require a window, allow the metal oxide to remain suspended and simplify the design required for continuous operation. On the other hand, care must be put into the design of the surfaces interacting with radiation as heat transfer limitations can render the reactor useless (Valades-Pelayo et al., 2015). Some designs consider a two cavity reactor (Steinfeld et al., 1998a, 1998b), a tubular nozzle (Abanades and Flamant, 2007), or multitubular arrays (Rodat et al., 2009a, 2009b).

Tubular reactor designs have proven to be robust, being able to operate at temperatures ranging 1400–2500 K (Rodat et al., 2009a, 2009b; Brkic et al., 2016a, 2016b; Valades-Pelayo et al., 2015). This presents an advantage for the reduction step, as high-temperatures lead to high thermal efficiency and low reaction times under continuous operation. In this regard, Brkic et al. (2016a, 2016b), reported conversions of 44% during the continuous reduction of aerosolized ZnO particles in a vertical tube reactor for residence times of 1 s. Temperatures of 2000 K and pressures 1–1000 mbar were investigated. Scheffe et al. (2014) conducted CeO_2 reduction in an electrically heated tubular reactor using small particles (100 nm to 100 μm). In this study, a downward aerosol flow of ceria particles counter to an argon sweep gas at 1900 K was considered. This resulted in conversions up to 40% above the measured equilibrium for reaction times of about 1 s.

Regarding modeling of suspended solar reactors, the work of Rodat et al. (2009a, 2009b) used the Dsmoke software to develop a detailed chemical kinetic simulation of the methane decomposition in a tubular reactor for a wide range of alkane transformations. Charvin et al. (2008), extended the work of Rodat et al. to a dynamic simulation considering continuous operation and transient periods, neglecting temperature gradients inside the reaction chamber and modeling the cavity receiver as a blackbody. Valdés-Parada et al. (2011) performed a numerical simulation for the same reactor model. The velocity, concentration and temperature profiles inside the reaction zone were determined as a function of the concentration and flow of gas at the entrance of the reactor. Radiative considerations are not discussed, however, model predictions fit in well with the experimental data presented by Rodat et al. (2009a, 2009b). Bader et al. (2015) proposed a solar packed-bed multi-tubular reactor concept for continuous fuel production via isothermal partial redox cycling of Ceria (Bader et al., 2013). The reactor geometry and operating conditions were specified based on a heat and mass transfer model. Temperature and stress distributions are predicted at an operating temperature of 1773 K, while considering measured rate data rather than chemical equilibrium projections of fuel production.

Some other studies consider a detailed description of the radiative heat transfer phenomena for particle suspensions coupled to chemical reaction kinetics, while neglecting other heat and mass transfer phenomena. For instance, Villafan-Vidales et al. (2009) simulated the radiative heat transfer in a solar thermochemical reactor for the thermal reduction of cerium oxide using the Monte Carlo method. The directional, spectral and power distributions of the concentrated solar radiation entering the cavity are considered. The suspension is treated as a non-isothermal, non-grey, absorbing, emitting, and anisotropically scattering medium. The optical properties of the particles are obtained from Mie-scattering theory by using the optical properties of cerium oxide (Özer, 2001; Wiktorczyk and Oles, 2007; Santa et al., 2004). A few studies focused on the experimental determination and modeling of effective radiative properties of CeO_2 ceramics can be found in the literature, such as the work of Ganesan et al. (2013). A detailed study regarding the effect of macropore structure of CeO_2 particles on their optical properties was presented by Wheeler et al. (2014).

Other works consider steady state radiative heat transfer using the discrete ordinates methods, or transient models based on the Rosseland approximation (Osinaga et al., 2004; Dombrovsky et al., 2007). Villafán-Vidales et al. (2011) modeled the steady state for a suspended SnO_2 particle-cloud, considering a thermal reduction reaction, radiative heat transfer by using the Monte Carlo method and convection. Martinek et al. (2012) presents a model that accounts for radiative heat transfer using the Monte Carlo method, mass transfer and chemical kinetics in a reactor for steam gasification of carbon, where thermophoresis is considered. Recently, Valades-Pelayo et al. (2015) presented a numerical study based on an indirectly irradiated multitubular reactor employing a radiative heat transfer model and a global optimization algorithm that helped define an optimized array for the vertical tubes within the cavity. The optimized array, allows close-to-isothermal operation of all tubes at 2785 K. Additionally, virtually no thermal stress is expected under the conditions of the IER-UNAM Solar Furnace (Perez-Enciso et al., 2014; Riveros-Rosas et al., 2010).