Solar Energy Materials & Solar Cells 160 (2017) 174–181

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Modeling of double-loop fluidized bed solar reactor for efficient thermochemical fuel production

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ARTICLE INFO

Keywords:
Fluidized bed
Solar reactor
Syngas
Cerium oxide
Nanoparticles

ABSTRACT

A new model of solar reactor based on a double-loop fluidized bed involving CeO_2 nanoparticles and two gas streams, N_2 and CO_2, for efficient thermochemical fuel production, is presented. The fluidized bed reactors are commonly used to carry out a variety of chemical reactions, due to solid granular materials, which play the fundamental role of catalyst. In the system under investigation, the overall reaction $CO_2 \rightarrow CO + 1/2 O_2$ is achieved, by means of a thermochemical two-step cycle, based on CeO_2 nanoparticles. The first step (CeO_2 thermal reduction) has been implemented with a solar-driven endothermic dissociation of the metal oxide to lower-valence metal-oxide. The second step (CO_2 splitting) has been carried out with an exothermic oxidation of the reduced metal-oxide, which is produced in the first step, to form CO. The use of nanoparticles as catalyst allows maximizing the surface area of reaction, and at the same time, the reactor based on double-loop fluidized bed allows continuous operation, without alternating flows of inert sweep gas and CO_2. The thermodynamic analysis of the system under investigation showed a calculated maximum ideal efficiency of about 63%.

1. Introduction

According to the Intergovernmental Panel on Climate Change, atmospheric concentration of carbon dioxide (CO_2) has to be stabilized at or below 450 ppm [1] and global CO_2 emissions must be reduced of 50% from 2006 levels by 2050, 100% by 2075, and beyond 100% by 2100 [2]. In order to reach these goals, in the next decades, all CO_2 sources have to be minimized, as well as the removal of CO_2 from the atmosphere will be necessary.

In this scenario, syngas, that is a mixture of H_2 and CO, can represent one of the most promising sustainable energy carriers when produced from renewable resources [3].

Today, syngas production methods include mainly steam reforming of natural gas or liquid hydrocarbons to produce hydrogen and gasification of coal, biomass or waste [4,5]. Furthermore, several processes of syngas production, based on solar energy as heat source, have been developed in the last decades [6,7]. Particularly, the thermochemical two-step cycles, based on metal oxides, represent a valid option for syngas production, due to their lower temperature (< 1700 K) compared to other processes. In this kind of process, the first step (thermal reduction) is developed through a solar-driven endothermic dissociation of the metal oxide to elemental metal or lower-valence metal-oxide. The second step (CO_2 splitting) is constituted by an exothermic oxidation of the reduced metal-oxide, which is produced in the first step, to form CO [3]. The overall reaction of the two-step cycle is the following:

$$CO_2 \rightarrow CO + 1/2 O_2 \tag{1}$$

In order to select the best metal-oxide, able to improve the reaction (1), many materials have been investigated, such as ferrites, zinc oxide, etc. [8–10]. According to Chueh et al. [11], the cycles based on ferrites suffer the sintering process and present slow kinetics [12–19], as well as zinc oxide based cycles require rapid quenching because of volatilization [20–22]. Recent studies on thermochemical dissociation of CO_2 focused their attention on ceria (CeO_2) as active material for CO_2 splitting reaction, because it has an extremely high melting temperature of approximately 2800 K and shows high catalytic activity towards carbon-containing gases [23–28].

Cerium Oxide is largely investigated in literature for its structural, chemical and optical properties that make it a promising material in several fields of applications, such as gas sensing, high refractive index material, fuel cells, catalysis, CO_2 adsorbing materials, nanofluids etc. [29–31]. Furthermore, Milanese et al. [32] demonstrated that the CeO_2 preserves its optical properties, even after several runs of thermal processes.

With the purpose to use solar energy as heat source, coupled with the above-described thermochemical two-step cycle, in the last years several innovative reactor designs have been proposed. Haueter et al.

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http://dx.doi.org/10.1016/j.solmat.2016.10.028
Received 7 July 2016; Received in revised form 17 October 2016; Accepted 18 October 2016
Available online 27 October 2016
0927-0248/

Nomenclature

C	heat capacity [J/K];
Cp	specific heat capacity [J/(kg·K)];
d_p	mean diameter of the clusters of nanoparticles [m];
g	gravitational acceleration [m/s^2];
$\dot{H}_{red}$	thermal power of reduction [W];
$\dot{H}_{ox}$	thermal power of oxidation [W];
$\dot{H}_{sun}$	sun power [W];
$\dot{H}_u$	useful power [W];
LHV_{CO}	low heating value [J/kg];
m	mass [kg];
m_{st}	stoichiometric mass [kg];
$\dot{m}$	mass flow rate [kg/s];
M	molar mass [kg/mol];
R	gas constant [J/(K mol];
S	surface [m^2];
$\bar{t}$	mean residence time [s];
T	temperature [K];
U_f	fluidization velocity [m/s];
U_{mf}	minimum fluidization velocity [m/s];
Δm	reduction on mass [kg];
η_g	ideal global efficiency;
μ	dynamic viscosity [Pa s];
ρ	density [kg/m^3].

[33] studied a rotating-cavity solar reactor for thermal dissociation of ZnO to Zn and O_2 at 2300 K, consisting of a rotating conical cavity-receiver that contains a quartz window for access of concentrated solar radiation. In this reactor, ZnO particles are continuously fed, while the gaseous products Zn(g) and O_2 are swept out by a continuous flow of inert gas to a quench device. Another design of a solar chemical reactor for the thermal dissociation of ZnO at above 2000 K has been presented by Schunk et al. [34].

Furler et al. [35,36] performed an experimental campaign at the High-Flux Solar Simulator of ETH Zurich, confirming the feasibility of a ceria-based cavity reactor. Particularly they built up a solar cavity-receiver containing porous ceria felt, directly exposed to concentrated thermal radiation at mean solar flux concentration ratios of up to 3015 suns. They experimentally realized several gas splitting cycles, yielding a solar-to-fuel energy conversion efficiency, defined as the ratio of the calorific value of CO (fuel) produced to the solar radiative energy input through the reactor's aperture and the energy penalty for using inert gas, equal to 1.73% average and 3.53% peak.

In order to improve the efficiency of this kind of systems, Bader et al. [37] presented a design of solar thermochemical reactor based on beds of millimetric porous ceria particles, contained in the annulus of concentric alumina tube assemblies that lined the cylindrical wall of a solar cavity receiver. The porous particle beds provided high surface area for the reactions, rapid heat and mass transfer and low pressure drop. In this system, redox cycling was accomplished by alternating flows of inert sweep gas and CO_2 through the bed.

Ermanoski et al. [38] describe and analyze the efficiency of a different solar-thermochemical reactor concept, which employs a moving packed bed of reactive particles, producing H_2 or CO from solar energy and H_2O or CO_2. The packed bed reactor combines several features, essential to achieve high efficiency: spatial separation of pressures, temperature and reaction products in the reactor, solid–solid sensible heat recovery between reaction steps, continuous on-sun operation and direct solar illumination of the working material. They show that in a fully developed regime, using CeO_2 as a reactive material, the conversion efficiency of solar energy into H_2 and CO at the design point can exceed 30%.

In order to further increase the surface area of reaction, nanoparticles can be used instead of millimetric particles. The interest in using nanoparticles in solar thermal collectors and in particular in direct absorption solar collectors is growing in the scientific community [39–45]. Recently, de Risi et al. [46] proposed and developed a transparent parabolic through collector (TPTC), working with gas-based nanofluids, for high-temperature applications. Transparent receivers combined with gas-based nanofluids were found to be able to directly adsorb solar radiation due to the very high total surface of nanoparticles.

In the present work, a new model of solar reactor, based on a double-loop fluidized bed, involving CeO_2 nanoparticles (*NPs*) and two gas streams (N_2 and water-vapor/CO_2), is presented. According to [37,38] the use of *NPs* as catalyst allows maximizing the surface area for the reactions, but differently from the previous works, the reactor, based on a double-loop fluidized bed, allows continuous operation, without alternating flows of inert sweep gas and CO_2.

2. Description of the system

Syngas can be produced from CO_2 by means of 2-step thermochemical cycle, based on CeO_2, according to the following chemical reactions [36].

$$\text{High temperature, } T > 1673\text{K}: CeO_2 \xrightarrow[\dot{H}_{red}]{} CeO_{2-\delta} + \frac{\delta}{2}O_2 \tag{2}$$

$$\text{Low temperature, } T < 1673\text{K}: CeO_{2-\delta} + \delta CO_2 \xrightarrow[-\dot{H}_{ox}]{} CeO_2 + \delta CO \tag{3}$$

In the first reaction, which happens at high-temperature (T > 1673 K), ceria is reduced to a non-stoichiometric state. In the second step, at lower temperature, ceria is re-oxidized with CO_2 producing CO.

In order to efficiently realize the reactions (2) and (3), a new model of double-loop fluidized bed solar reactor, involving CeO_2 *NPs* and two gas streams (N_2 and CO_2) is proposed. Fig. 1 shows a schematic model of the double-loop fluidized bed solar reactor under investigation.

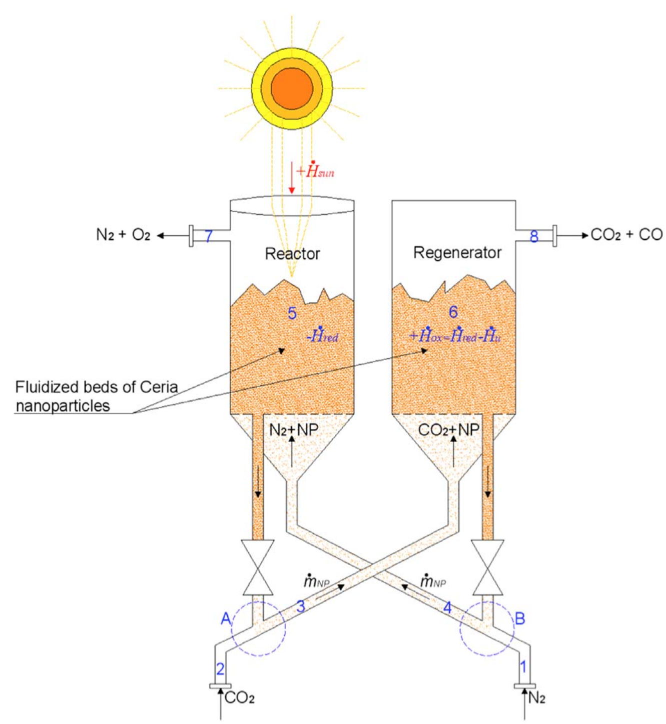

Fig. 1. Schematic model of double-loop fluidized bed solar reactor.