Solar Energy 155 (2017) 363–371

Contents lists available at ScienceDirect

Solar Energy

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

Modeling of ammonia synthesis to produce supercritical steam for solar thermochemical energy storage

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ARTICLE INFO

Article history:
Received 1 March 2017
Received in revised form 12 June 2017
Accepted 17 June 2017

Keywords:
Concentrating solar power
Thermochemical energy storage
Ammonia synthesis
Supercritical steam

ABSTRACT

In ammonia-based solar thermochemical energy storage systems, solar energy is stored by production of hydrogen (H_2) and nitrogen (N_2) via ammonia dissociation and released when the hydrogen and nitrogen react exothermically to heat a working fluid for electricity generation. In our lab, a concentric-tube ammonia synthesis reactor has been built with steam in the tube and ammonia synthesis in the shell packed with a porous bed of iron catalyst. It achieves heating of supercritical steam at ~26 MPa from ~350 °C to ~650 °C; to our knowledge this is the first time that ammonia synthesis has been used to heat steam to a sufficiently high temperature for a supercritical steam power block. In this paper, a model is proposed to simulate heating of supercritical steam in an ammonia synthesis reactor. The model is a two-dimensional, steady-state, pseudo-homogeneous, packed bed reactor computational model that solves the energy and mass species conservation equations, along with the Temkin-Pyzhev rate equation. The model results for temperature distributions match well with experimental results from our reactor. A sensitivity analysis is carried out for the model to study the effects of six input parameters on the gas and steam temperature profiles. The results show the process in our reactor is heat-transfer-limited and most sensitive to activation energy. The process is also very sensitive to inlet ammonia mass fraction. Improving heat transfer and decreasing inlet ammonia mass fraction are crucial to improve the capability of the reactor to heat a higher steam mass flow rate per unit of synthesis gas mass flow rate.

1. Introduction

In order to advance concentrating solar power technology, there is a need for thermal energy to be stored during the daytime and recovered on demand. Thermal energy storage systems can be categorized as sensible heat, latent heat, and thermochemical energy storage. In commercial solar thermal power systems, thermal storage is currently dominated by sensible heat storage in tanks of molten salts. Thermochemical energy storage technology utilizes reversible chemical reactions, i.e. energy is stored in chemical bonds during the endothermic reaction step and released during the exothermic one. Compared with the other two types, thermochemical energy storage has the potential for higher energy density, minimal energy losses during the storing operation (Abedin and Rosen, 2011; Pardo et al., 2014), capability of being stored as long as desired at ambient temperature (Ervin, 1977), and ability for the power block to operate at high efficiency with almost constant-temperature discharging (Strohle et al., 2016).

Among many kinds of thermochemical energy storage technologies, e.g. metal hydrides (Felderhoff and Bogdanovic, 2009), carbonation/decarbonation systems (Kyaw et al., 1996), or CO_2 reforming of methane (Worner and Tamme, 1998), the ammonia dissociation and synthesis energy storage system, with 40 years of research, is the most mature (Pardo et al., 2014). Fig. 1 shows a schematic of an ammonia-based solar thermochemical energy storage system. The enthalpy of reaction is 66.6 kJ/mol (Sandler, 2006) at temperature of 300 K and pressure of 30 MPa. Note that high operating pressure is used in this system to shift the equilibrium curve to higher temperature, allowing operation of the exothermic reaction at higher temperatures with consequently higher reaction rates (Lovegrove, 1993). In the system, ammonia (NH_3) is dissociated endothermically as it absorbs solar energy during the daytime. The stored energy can be released on demand when the hydrogen (H_2) and nitrogen (N_2) react exothermically to synthesize ammonia. The released thermal energy can be used to heat a working fluid (supercritical steam in this study). Further, the working fluid can power a turbine to generate electricity. Our larger research objective, of which this paper reports a part, is to show that ammonia-based thermochemical energy storage can

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http://dx.doi.org/10.1016/j.solener.2017.06.049

Nomenclature

c_p	specific heat capacity, J/(kg·K)
D_{eff}	catalyst bed effective diffusivity, m^2/s
D_h	hydraulic diameter, m
E_a	activation energy, J/mol
f_{NH3}	ammonia mass fraction
h	heat transfer coefficient, W/m^2·K
ΔH	heat of reaction, J/kg
$k_{o,m}$	pre-exponential constant, kg/(m^3·s)
k_s	steam thermal conductivity, W/(m·K)
K_p	equilibrium constant
k_{eff}	catalyst bed effective thermal conductivity, W/(m·K)
k_{series}	thermal conductivity of series mechanism in solid phase, W/(m·K)
k_w	wall thermal conductivity, W/(m·K)
L	reactor length, m
$\dot{m}$	mass flow rate, kg/s
Nu	Nusselt number
P	gas total pressure, Pa
P_j	partial pressure, where j indicates species, NH_3, N_2, or H_2, Pa
P_o	standard state pressure, 1 atm
q''_w	wall heat flux, W/(m^2·K)
r	radial coordinate, m
$\dot{r}'''$	rate of ammonia synthesis, kg/(m^3·s)
Re_p	poarticle Reynolds number
R_u	universal gas constant, J/(mol·K)
T	temperature, °C
U	overall heat transfer coefficient, W/(m^2·K)
v	velocity, m/s
x	axial coordinate, m

Greek letters

α	parameter in Temkin-Pyzhev rate equation
ε	porosity
η	effectiveness factor in Temkin-Pyzhev rate equation
ρ	density of the gas mixture (kg/m^3)

Subscripts

1	at annulus inner radius
2	at annulus outer radius
c	center
cond	conduction
conv	convection
exp	experimental
eq	equilibrium
g	reacting gas mixture
i	inner
in	inlet
ins	insulation
m	model
max	maximum
o	outer
out	outlet
pred	predicted
rad	radiation
s	steam
w	wall

meet the Department of Energy SunShot target to heat a working fluid to 650 °C at a storage system specific capital cost below $15/kWh$_t$.

Ammonia-based thermochemical energy storage ("ammonia-based TCES") for concentrating solar power systems has been studied and investigated since 1974 (Dunn et al., 2012). Subsequently, much progress has been made on demonstrating the feasibility of ammonia-based TCES, e.g., Lovegrove et al. built and tested a 1 kW$_{sol}$ closed loop system (Lovegrove et al., 1999) and a 15 kW$_{sol}$ ammonia-based TCES system for dish power plants (Lovegrove et al., 2004). Their systems demonstrated ammonia dissociation on a dish concentrator and subsequent energy recovery at temperatures high enough for electricity generation, but did not demonstrate heating of a working fluid. Commercial ammonia plants using the Haber Bosch process typically recover exothermic reaction heat as steam at around 450 °C. Before the present work, ammonia synthesis had not (to our knowledge) been shown to reach temperatures consistent with modern power blocks such as a supercritical steam Rankine cycle requiring supercritical steam to be heated to ~650 °C at 26 MPa (Naidin, 2009). In Chen et al. (2016a), we demonstrated the feasibility of the concept of heating supercritical steam to 650 °C by showing that the maximum temperature of the synthesis reaction in our experiment was higher than 650 °C. In the present paper, a simulation model is presented for utilizing the ammonia synthesis reaction to heat supercritical steam at 26 MPa from 350 to 650 °C. Further, the model is validated by comparing with experimentally measured temperatures. A sensitivity analysis is carried out on six of the input parameters in the model.

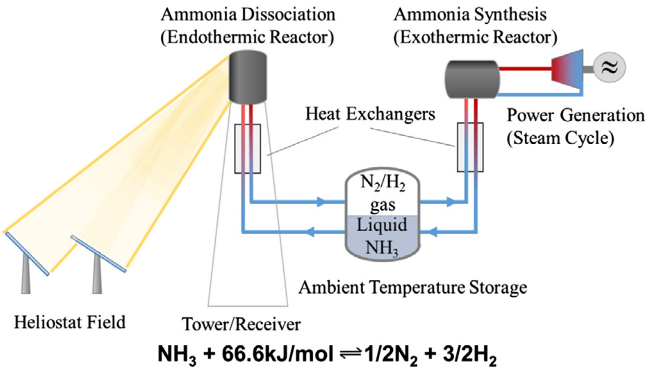

Fig. 1. Schematic of an ammonia-based thermochemical energy storage system including ammonia dissociation, storage, and synthesis sub-systems.

2. Reactor model

A pseudo-homogeneous steady-state model originally developed by Richardson et al. (1988) is used to simulate the reaction kinetics and thermodynamics of reacting gas in the catalytic bed. The pseudo-homogeneous steady state model is very commonly employed for designing packed bed reactors (Hill, 1977; Ramkrishna and Arce, 1989). The model has been modified and validated by Lovegrove and others at Australian National University for ammonia dissociation and synthesis (Kreetz and Lovegrove, 1999; Lovegrove, 1996). Chen et al. (2016b) further improved the model with the capability of simulating heat transfer between the reaction in the bed and a secondary working fluid. In this model, the catalyst bed is treated as a continuum with averaged properties, i.e. effective conductivity (k_{eff}) and effective diffusivity (D_{eff}) (Richardson et al., 1988). Also, the model assumes: (1) axial conduction is negligible, (2) gas pressure is constant for purposes of evaluating properties and reaction rate, (3) radial velocity is