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1 kW_e sodium borohydride hydrogen generation system Part II: Reactor modeling

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Abstract

Sodium borohydride ($NaBH_4$) hydrogen storage systems offer many advantages for hydrogen storage applications. The physical processes inside a $NaBH_4$ packed bed reactor involve multi-component and multi-phase flow and multi-mode heat and mass transfer. These processes are also coupled with reaction kinetics. To guide reactor design and optimization, a reactor model involving all of these processes is desired. A one-dimensional numerical model in conjunction with the assumption of homogeneous catalysis is developed in this study. Two submodels have been created to simulate non-isothermal water evaporation processes and pressure drop of two-phase flow through the porous medium. The diffusion coefficient of liquid inside the porous catalyst pellets and the mass transfer coefficient of water vapor are estimated by fitting experimental data at one specified condition and have been verified at other conditions. The predicted temperature profiles, fuel conversion, relative humidity and pressure drops match experimental data reasonably well.

Keywords: Sodium borohydride; Reactor modeling; Porous media; Multi-phase

1. Introduction

A sodium borohydride hydrogen generator is unique because both reactants can be stored together, and hydrogen is generated by passing sodium borohydride solution through a catalyst bed to initiate hydrolysis reaction as [1]:

$$NaBH_4 + 2H_2O \xrightarrow{\text{Catalyst}} NaBO_2 + 4H_2 + \text{Heat} \quad (1)$$

The effects of catalysts, pH and temperature on sodium borohydride hydrolysis reaction were discussed in Ref. [2]. Our experimental paper [3] discussed system-level experiments on a 1 kW_e sodium borohydride hydrogen generator and exposes solubility issues that may limit the maximum usable concentration to approximately 15%, which may preclude automotive applications; nevertheless, sodium borohydride systems may still find applications in portable electronic devices and other niche areas [4,5]. Most prior work on sodium borohydride systems has focused on experimental testing, and no work on system-level reactor modeling has been reported to date. The processes in the reactor are quite complex, involving multiple components ($NaBH_4$, NaOH, $NaBO_2$, H_2O, H_2) and multiple phases (liquid and gas). In addition, general liquid phase reactions inside a packed bed reactor accompanied by significant water evaporation have not received attention in the literature. As a result, a significant need exists for a sodium borohydride hydrolysis reactor model to enable reactor design and optimization. The development of such a reactor model will also facilitate the study of hydrogen storage systems using other chemical hydrides. Thus motivated, we have developed a one-dimensional numerical model in conjunction with the assumption of homogeneous catalysis and have validated this model with experimental data.

2. Experiments

A 1 kW_e sodium borohydride hydrogen generation system (by assuming a fuel cell efficiency of 50%) has been established for system-level studies. The 1 kW_e hydrogen generation apparatus was described in detail in a previous paper [3] and is only summarized here. Fig. 1 shows the section view of the

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Nomenclature

a_g external surface area per volume of catalytic bed ($m^2\, m^{-3}$) = $6(1-\varepsilon)/d_p$ for packed bed ($m^2\, m^{-3}$)
A_t cross-sectional area of the reactor (m^2)
$c_{p,f}$ specific heat of the fuel ($kJ\, kg^{-1}\, k^{-1}$)
C_A molar concentration of species A in the fluid ($kmol\, m_f^{-3}$)
d_p particle diameter, equivalent diameter of sphere of the same external surface area (m)
d_t internal tube diameter of the reactor (m_r)
$D_{l,A,e}$ effective liquid diffusivity inside the catalyst at temperature T ($m_f^3\, m_p^{-1}\, s^{-1}$)
$D_{l,A}$ liquid diffusivity inside the catalyst at temperature T ($m_f^3\, m_p^{-1}\, s^{-1}$)
$D_{l,A,0}$ liquid diffusivity inside the catalyst at temperature T_0 ($m_f^3\, m_p^{-1}\, s^{-1}$)
E_{act} activation energy for sodium borohydride hydrolysis on ruthenium catalyst (66,900 $kJ\, kmol^{-1}$)
f_{TP} two-phase factor (2.3 was used in current study)
h_{fg} heat of vaporization of water, assumed to be constant 2250 $kJ\, kg^{-1}$ or 40,500 $kJ\, kmol^{-1}$
ΔH_{ads} heat of reaction for the adsorption of borohydride ion on the surface of ruthenium catalyst (−35,000 $kJ\, kmol^{-1}$)
ΔH_{rxn} heat of reaction for the sodium borohydride hydrolysis (−210,000 $kJ\, kmol^{-1}$)
k_L reaction rate coefficient for Langmuire–Hinshelwood kinetic model ($kmol\, kg\, cat^{-1}\, s^{-1}$)
k_l mass transfer coefficient from liquid to solid interface, based on concentration driving force ($m_f^3\, m_i^{-2}\, s^{-1}$)
k_{H_2O} mass transfer coefficient for water vapor (m^{-1})
K isotherm adsorption coefficient for borohydride ion on the surface of the catalyst ($m^3\, kmol^{-1}$)
L length of the reactor (m)
$\dot{m}_f$ mass flow rate of sodium borohydride solution ($kg\, s^{-1}$)
$\dot{m}_{f,0}$ initial mass flow rate of sodium borohydride solution ($kg\, s^{-1}$)
MW_{H_2} molecular weight of hydrogen ($kg\, kmol^{-1}$)
MW_{H_2O} molecular weight of water ($kg\, kmol^{-1}$)
$\dot{n}_B$ molar flow rate of liquid water ($kmol\, s^{-1}$)
$\dot{n}_C$ molar flow rate of hydrogen ($kmol\, s^{-1}$)
$\dot{n}_D$ molar flow rate of water vapor carried with hydrogen stream ($kmol\, s^{-1}$)
n'_{evap} total rate of water vaporization per unit catalyst mass ($kmol\, water\, kg\, cat^{-1}\, s^{-1}$)
$n'_{evap,1}$ rate of water vaporization corresponding to the generation of hydrogen per unit catalyst mass ($kmol\, water\, kg\, cat^{-1}\, s^{-1}$)
$n'_{evap,2}$ rate of water vaporization corresponding to mass transfer from catalyst surface to the bulk gas stream per unit catalyst mass ($kmol\, water\, kg\, cat^{-1}\, s^{-1}$)
P_{back} backpressure of the reactor (bar)
$P_{sat,H_2O}(T)$ saturation pressure of water vapor at temperature T (bar)
P_t total pressure of the reactor at location z (bar)
ΔP_{fritz} total pressure drop across the fritzs (Pa, psi)
ΔP_{total} total pressure drop across the reactor (Pa, psi)
r'_A rate of reaction per unit catalyst mass ($kmol\, kg\, cat^{-1}\, s^{-1}$)
$Re_l = d_p \rho_l u_s/\mu_l$ Reynolds number of the liquid phase
R universal gas constant, 8.314 ($kJ\, kmol^{-1}\, K^{-1}$)
RH relative humidity of hydrogen stream
S_{pellet} the external surface area of the pellet (m^2)
T temperature in the reactor at location z (K)
T_∞ ambient temperature (K)
$u_{l,s}$ superficial velocity of the liquid phase through the bed ($m\, s^{-1}$)
$u_{g,s}$ superficial velocity of the gaseous phase ($m\, s^{-1}$)
$\bar{u}$ average velocity of the multi-phase fluid across the reactor ($m\, s^{-1}$)
$\dot{V}_g$ volumetric flow rate of the gaseous phase (m^3)
V_{pellet} the volume of the pellet (m^3)
W_f total mass flow rate of the liquid phase ($kg\, s^{-1}$)
W_g total mass flow rate of the gas phase ($kg\, s^{-1}$)
W_{total} total mass flow rate of the multi-phase fluid ($kg\, s^{-1}$)
x_A conversion of sodium borohydride
$x_{quality}$ fraction of the gas phase out of the multi-phase fluid
z axial direction (m)

Greek letters
ε void fraction of packing in a packed bed ($m_f^3\, m_r^{-3}$)
ε_s internal void fraction of the catalyst pellet, between 0.3 and 0.8, typically 0.40
ϕ thiele modulus number for cylinder
η_G overall effectiveness factor
η effectiveness factor
μ_l liquid viscosity at temperature T ($kg\, m^{-1}\, s^{-1}$)
$\mu_{l,0}$ liquid viscosity at temperature T_0 ($kg\, m^{-1}\, s^{-1}$)
ρ_b catalyst bulk density in a packed bed ($kg\, m^{-3}$)
ρ_f fluid density ($kg\, m^{-3}$)
ρ_g density of the gaseous phase ($kg\, m^{-3}$)
ρ_s density of catalyst ($kg\, cat\, m_p^{-3}$)
ρ_{H_2} density of the hydrogen gas ($kg\, m^{-3}$)
$\rho_{H_2O\, vapor}$ density of the water vapor ($kg\, m^{-3}$)
$\bar{\rho}$ weighted average density of the multi-phase fluid ($kg\, m^{-3}$)
τ tortuosity factor, typically 3.0 to 4.0

Subscripts
0 initial condition
A sodium borohydride
b bulk phase
B liquid water
C hydrogen