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Production of hydrogen via an Iron/Iron oxide looping cycle: Thermodynamic modeling and experimental validation

A. Singh, F. Al-Raqom, J. Klausner, J. Petrasch*

Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, USA

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ABSTRACT

An incremental thermodynamic equilibrium model has been developed for the chemical reactions driving a clean, hydrogen producing iron/iron oxide looping cycle. The model approximates a well-mixed reactor with continuous reactant gas flow through a stationary solid matrix, where the gas residence time is long compared to time constants associated with chemical kinetics and species transport. The model, which computes the theoretical limit for steam-to-hydrogen conversion, has been experimentally validated for the oxidation reaction using an externally heated, 21 mm inner diameter, tubular fluidized bed reactor. Experiments were carried out at 660 and 960 °C with steam flow rates ranging from 0.9 to 3.5 g/min. For small flow rates, i.e., for long residence times, the experimentally observed cumulative steam-to-hydrogen conversion approaches the theoretically predicted conversion. At a 960 °C operating temperature, the measured hydrogen yield approaches the theoretical limit (experimental yields are always within 50% of the theoretical limit), and the yield is insensitive to variations in the steam flow rate. In contrast, the measured hydrogen yield deviates significantly from the theoretical limit at a 660 °C operating temperature, and strong variations in hydrogen yield are observed with variations in steam flow rate. This observation suggests that the reaction kinetics are significantly slower at lower temperature, and the model assumption is not satisfied.

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1. Introduction

The solar thermochemical production of fuels such as hydrogen or Syngas using metal/metal oxide looping processes [1–3] is considered an interesting route to carbon-neutral fuels. The concept shows promise in helping to satisfy a growing global energy demand, reducing oil price volatility, and mitigating anthropogenic climate change. Solar driven looping processes use water and CO₂ as the sole feedstocks and concentrated solar radiation as the sole energy source. Looping processes using natural gas [4–7] or coal-

derived Syngas [8,9] as the reducing agent constitute an important stepping-stone toward carbon-neutral hydrogen production. This study uses iron/iron oxide redox pairs as the reactive material [10]. This process is capable of producing significantly higher purity hydrogen than conventional coal gasification and subsequent water gas shift [11,12]. Another advantage is that the process avoids gas-phase separation. Metallic iron is oxidized by steam, producing hydrogen and iron oxides during the first reaction step. Coal-derived Syngas is then passed through the oxides, reducing them back to iron during the second reaction step. Since the gaseous products of

* Corresponding author. University of Florida, Department of Mechanical and Aerospace Engineering, 330 MAE-B, Gainesville, FL 32611, USA. Tel.: +1 352 392 9129.

E-mail address: joerg.petrasch@fhv.at (J. Petrasch).

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Nomenclature			
c_p	Specific heat capacity, $\text{kJ kmol}^{-1} \text{K}^{-1}$	n_i	Number of moles for a species i , kmol
G	Gibbs free energy, kJ	$m_{\text{Fe,init}}$	Initial mass of iron, kg
\bar{g}_i^0	Reference Gibbs function of species i evaluated, kJ kmol^{-1}	P_{ref}	Reference pressure, N m^{-2}
h	Enthalpy, kJ kmol^{-1}	PID	Proportional-integral-derivative
\dot{m}	Mass flow rate, kg s^{-1}	R	Universal gas constant, $\text{kJ kmol}^{-1} \text{K}^{-1}$
M	Molar mass, kg kmol^{-1}	sLPM	Standard liters per minute
m_{Fe}	Mass of iron, kg	T	Temperature, K
P	Total system pressure, N m^{-2}	t	time, s
		$y_{i,\text{eq}}$	Mole fraction at equilibrium
		y_i	Species i mole fraction

the oxidation reaction consist of hydrogen and steam only, the process can generate highly pure hydrogen through steam condensation. Furthermore the reduction step yields highly concentrated CO_2 suitable for sequestration.

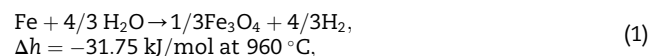
The suggested two-step process uses the same reactor for both the reduction and the oxidation reaction. The solid reactants remain in the reactor and streams of steam and Syngas are alternately fed to the reactors [9]. In contrast, the three-step steam-iron process [6,11–20] employs two separate reactors for hydrogen production and iron oxide reduction [21], hence necessitating the transport of hot solids between reactors.

To evaluate the theoretical potential of the suggested two-step process, an open system incremental thermodynamic equilibrium model is developed for both the hydrogen production (oxidation) step and the regeneration (reduction) step. The hydrogen production step is also carried out experimentally to study the validity of the thermodynamic model and to determine the conditions for its applicability. Roeb et al. [22] conducted a thermodynamic analysis for two-step water splitting with mixed iron oxides including nickel-iron-oxide and zinc-iron-oxide to evaluate the maximum hydrogen production potential of coating materials using FactSage software [23]. Their analysis showed that maximum hydrogen yield is realized when (i) the reduction temperature is raised to 1300°C , (ii) the water splitting temperature is lowered below 800°C , and (iii) the oxygen partial pressure during reduction is minimized. This is consistent with similar findings by Singh et al. [9]. Roeb et al. have also validated the effect of reduction temperature and oxygen partial pressure in experimental studies. However, they could not experimentally verify the increased hydrogen yield at lower water splitting temperatures of approximately 800°C . They concluded that kinetics play an important role in the oxidation step. Svoboda et al., have carried out a thermodynamic study of the potentials and limitations of iron based chemical looping processes for the production of high purity hydrogen. They studied the $\text{Fe}-\text{Fe}_3\text{O}_4$ system for cyclic hydrogen production in the temperature range of $400\text{--}800\text{ K}$ [8]. In their analysis, they have evaluated the hydrogen yield at equilibrium for the steam oxidation of pure iron to magnetite (Fe_3O_4). In accordance with Singh et al. and Roeb et al., [9,22] their theoretical results showed that lower oxidation temperatures are favorable for attaining higher hydrogen yields. They have also indicated that at lower temperatures, the reaction is limited by kinetics.

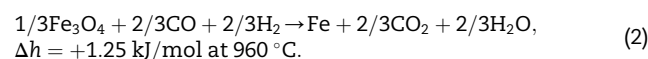
In the current study, an incremental thermodynamic equilibrium model is employed to predict the maximum attainable reaction yields. The model approximates a well-mixed reactor with continuous reactant gas flow through a stationary solid matrix where the gas residence time is long compared to time constants associated with chemical kinetics. The model is validated experimentally for the oxidation case using an externally heated tubular fluidized bed reactor. The current study is limited to the oxidation reaction of the looping cycle.

2. Thermodynamic analysis

The ideal two-step iron based looping process for the production of hydrogen consists of the hydrogen production step [2]:



followed by the reduction step:



High purity hydrogen and magnetite are produced during the first step. During the second step, magnetite is reduced back to iron using Syngas as the reducing agent. Coking and iron carbide formation may occur during reduction. These products may react with steam in the oxidation process producing CO , CO_2 , and CH_4 along with hydrogen. A detailed analysis of the by-products of the reduction reaction has been carried out in [9]. In the ideal process hydrogen is completely consumed in the reduction reaction. However, in real processes a large fraction of the hydrogen will not react. The hydrogen and CO_2 in the off-gases of the reduction step may be separated via conventional techniques, such as pressure swing absorption (PSA) [25] leading to lower purity hydrogen.

An open system equilibrium model (Fig. 1) for a single looping reactor is implemented. Small amounts of steam are added to the system and the ensuing equilibrium reactant gas mixture is removed from the system. Solid material remains within the system. Assuming constant temperature and pressure and ideal gas behavior, the species balance for a gaseous component follows:

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