Korean J. Chem. Eng., **24**(3), 527-531 (2007)

Chemical-looping hydrogen generation system: Performance estimation and process selection

Ho-Jung Ryu[†] **and Gyoung-Tae Jin**

Korea Institute of Energy Research, Daejeon 305-343, Korea

(*Received 30 August 2006 • accepted 4 November 2006*)

Abstract−To find a suitable metal component in an oxygen carrier particle for a chemical-looping hydrogen generation system (CLH), oxygen transfer capacities of metal components were investigated, and Ni was selected as the best metal component. The optimum operating conditions to have maximum hydrogen generation rate have been determined based on the chemical-equilibrium composition analysis in a water splitting reactor. Moreover, suitable compositions of syngas from a gasifier of heavy residue oil to provide high energy efficiency have been determined based on the heat of reaction. With the selected operating conditions, the best configuration of two interconnected fluidized beds system for the chemical-looping hydrogen generator has been devised.

Key words: Chemical-looping Hydrogen Generation System, CLH, Hydrogen, Carbon Dioxide

INTRODUCTION

Hydrogen is the cleanest recyclable fuel that produces only water when used as a fuel. Hydrogen is not a primary source of energy; it is an intermediary form or a secondary form of energy. In the hydrogen energy system, it is faced that hydrogen will be produced from non-fossil energy sources, and will be used in every application where fossil fuels are used today. Hydrogen production is the most fundamental part of the hydrogen energy system, and has always been the object of intense and vigorous research and development. World hydrogen production has been growing rapidly at 8-10% per annum for many years [1]. At present, hydrogen is produced mainly from fossil fuels, water and biomass. Especially, more than 90% of the hydrogen is produced from fossil fuels [2].

Most of the current hydrogen production technologies need an additional process such as a shift reaction to improve hydrogen yield and CO_2 separation process to separate almost pure hydrogen from the gas mixture of CO, CO_2, H_2, and methane. To separate CO_2 from the exhaust gas requires additional energy and equipment. More than 22% of hydrogen generation cost is for CO_2 separation to purify hydrogen [3].

A chemical-looping hydrogen generation system (CLH) is a novel hydrogen production technology with an inherent separation of CO_2. This system has the advantage of no energy penalty for separation of CO_2 and high hydrogen yield without any additional process. The chemical-looping hydrogen generation system consists of two reactors, a water splitting reactor and a reduction reactor, as shown in Fig. 1. A fuel and a steam go through the different reactors. Eqs. (1)-(4) illustrate the basic concept of the chemical-looping hydrogen generation system. In the reduction reactor, gaseous fuel (CH_4, H_2, CO, C_nH_{2n+2}, or syngas) reacts with metal oxide according to Eqs. (2)-(4), and releases water vapor and carbon dioxide from the top and metal particles (M) from the bottom. The solid products, metal particles, are transported to the water splitting reactor and react with steam, as shown in Eq. (1), producing hydrogen and metal oxide particles. Metal oxide particles are recycled to the reduction reactor and supply oxygen for the reduction reaction. Between the two reactors, metal (or metal oxide) particles play an important role in transportation of oxygen and heat; therefore, the looping material between the two reactors is termed an oxygen carrier particle.

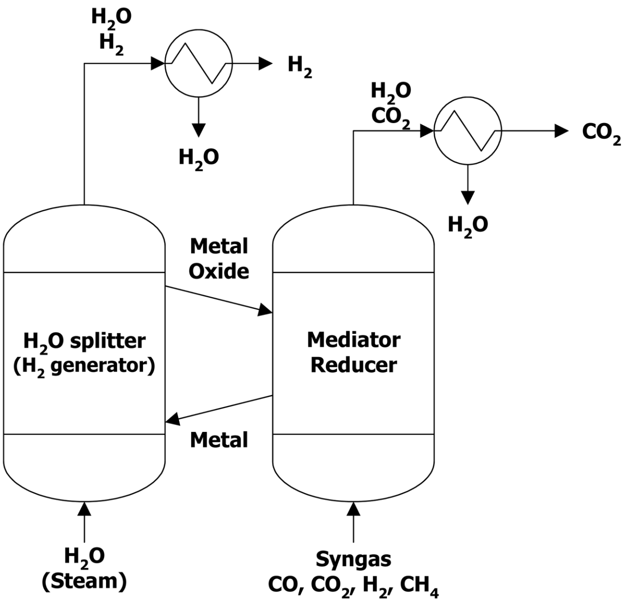

Fig. 1. Basic concept of chemical-looping hydrogen generation system.

It is important that the gas composition of the exhaust gas from the reduction reactor contains only highly concentrated CO_2 and water vapor. Therefore, CO_2 can be easily recovered by cooling the exhaust gas without any extra energy consumption for CO_2 separation. Moreover, the exhaust gas from the water splitting reactor contains only hydrogen and water vapor. After water condensation, al-

---

[†] To whom correspondence should be addressed.
E-mail: hjryu@kier.re.kr

[‡] This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

most pure hydrogen can be obtained with little energy loss for component separation.

Water splitting reaction	$M+H_2O \rightarrow MO+H_2$	(1)
Reduction reactor	$4MO+CH_4 \rightarrow 4M+CO_2+H_2O$	(2)
	$MO+H_2 \rightarrow M+H_2O$	(3)
	$MO+CO \rightarrow M+CO_2$	(4)

M: metal, MO: metal oxide

In this study, the performance of a chemical-looping hydrogen generation system and suitable process configuration have been determined by thermodynamic analysis for the water splitting and reduction reactions. For the thermodynamic analysis, the equilibrium composition of exhaust gas from the water splitting reaction and heat of reaction in the reduction reaction with variation of the operating conditions was determined. At a given operating condition, the Gibbs free energy of a system has to be minimum at equilibrium condition which is used to find the equilibrium composition for the reacting gaseous mixtures. The heat of reduction was calculated by the enthalpy change. In this study, a syngas from the heavy residue gasification was considered as a fuel to save fuel costs for a chemical-looping hydrogen generation system.

OXYGEN CARRIER PARTICLE

Recently, Ryu and Jin [4] proposed criteria for selection of metal component in oxygen carrier particles for a chemical-looping combustion (CLC) system. In their study, applicable metal components were selected based on the physical properties such as melting point and atomic or molecular weight. For the applicable metal components, possible reduced and oxidized phases were considered. Moreover, they investigated heat of reaction, oxygen transfer capacity, and crystal structures identified by the XRD analysis. As a conclusion, they found that Ni has appropriate heats of oxidation and reduction, excellent performance in oxygen transfer capacity, fixed reduced and oxidized phase (i.e., there is no other oxidized and reduced form except for NiO and Ni). Based on these results, we selected Ni particle as a base material for oxygen carrier in the chemical-looping hydrogen generation system [5,6].

OPERATING CONDITIONS

To determine the optimum operating conditions, temperature, pressure, mole ratio of nickel to steam, gas velocity, and solid circulation rate were varied and the equilibrium composition in the water splitting reactor and heat of reaction in the reduction reactor was determined.

The effect of temperature on the equilibrium composition in the water splitting reaction is shown in Fig. 2 where the steam-to-nickel ratio was fixed at 1 : 100 at 1 atm. As shown, only hydrogen and steam (water vapor) were produced from the water splitting reaction. After water condensation, almost pure H_2 can be obtained with little energy loss for purification or separation. The hydrogen yield increases with increasing the reaction temperature since water splitting is a highly endothermic reaction. In this study, the basis of the reaction temperature was 900 °C and the column diameters of water splitting reactor and reduction reactor were 0.1 m, respectively.

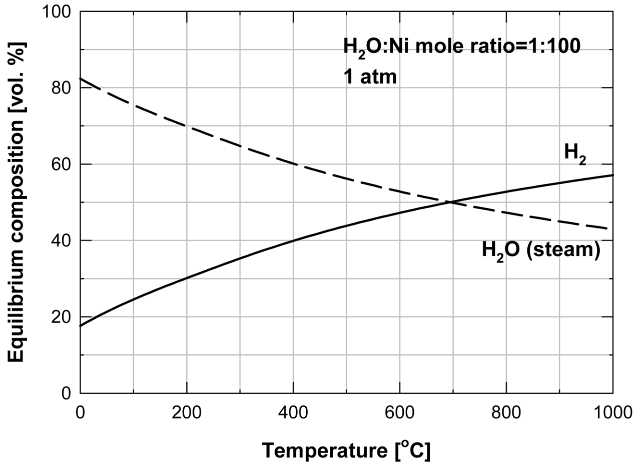

Fig. 2. Effect of temperature on the equilibrium composition in the water splitting reaction.

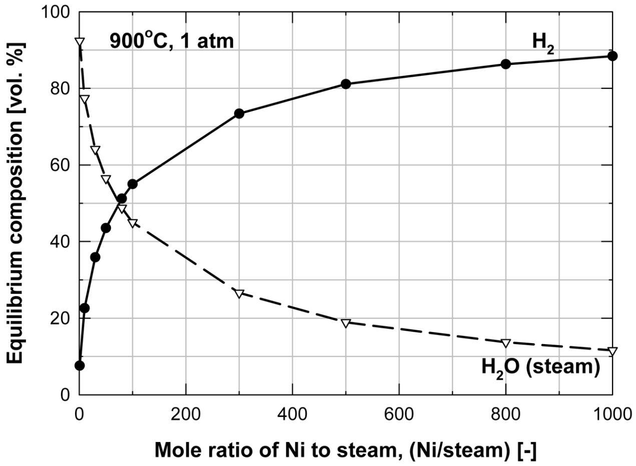

Fig. 3. Effect of the nickel-to-steam mole ratio on the equilibrium composition in the water splitting reaction.

Fig. 3 shows the effect of nickel-to-steam mole ratio on the equilibrium compostion in the water splitting reaction at 900 °C and 1 atm. The hydrogen yield increases as the nickel-to-steam mole ratio is increased. In a continuous chemical-looping hydrogen generation system, we can increase the mole ratio of nickel-to-steam by varying the solid circulation rate between the water splitting reactor and the reduction reactor. However, the maximum solid circulation rate will constrain the upper limit of hydrogen yield at a given operating condition. Another key to increasing the nickel-to-steam ratio is the composition of oxygen carrier particles. Most of the previous oxygen carrier particles have 60-70% of metal oxide in the particle. The higher metal oxide content affects the reaction rate of the oxygen carrier particles.

The effect of the system pressure (1-20 atm) on hydrogen yield in the water splitting reactor at 900 °C and steam-to-nickel ratio of 1 : 100 is shown in Fig. 4(a). As can be seen, the quilibrium composition is independent of pressure employed in this study. The reaction rate might increase with increasing the system pressure, but increasing the system pressure leads to increment of the steam-to-

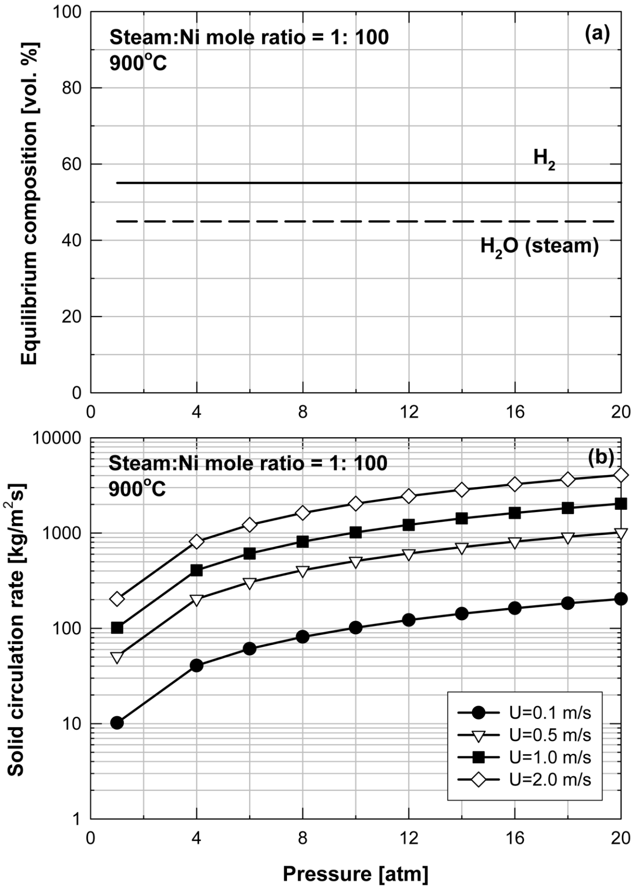

Fig. 4. Effect of system pressure on (a) equilibrium composition and (b) solid circulation rate.

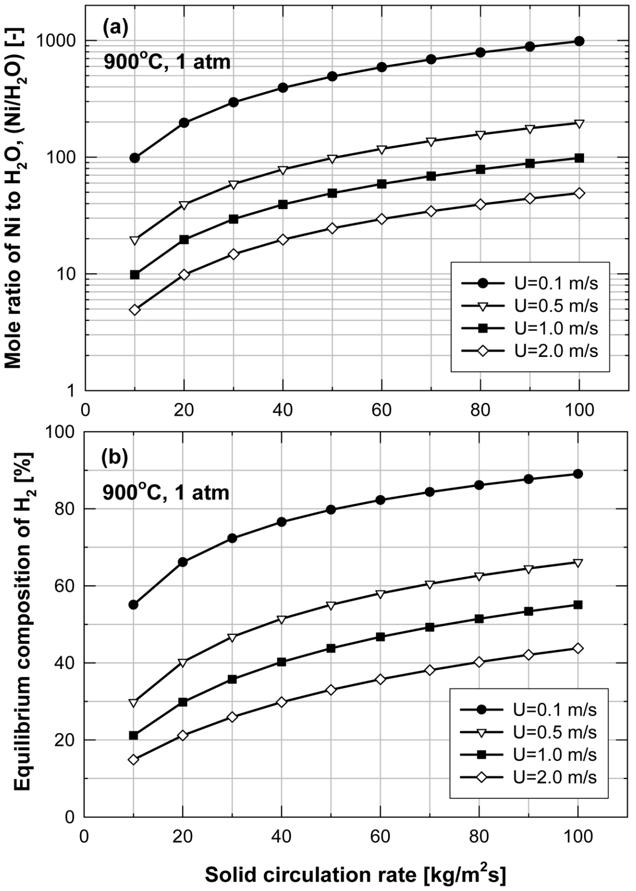

Fig. 5. Effect of solid circulation rate on (a) nickel-to-steam mole ratio and (b) equilibrium composition.

nickel mole ratio at the given mole of nickel and gas velocity. This result indicates that a higher solid circulation rate is needed to satisfy a given mole ratio of steam-to-nickel as the system pressure is increased. Fig. 4(b) illustrates how the system pressure affects the solid circulation rate between the water splitting reactor and the reduction reactor to satisfy a given steam-to-nickel mole ratio at a given steam input. The solid circulation rate increases with increasing the system pressure at a given steam velocity. The upper limit of the solid circulation rate in a commercial circulating fluidized bed is around 100 kg/m^{2}s [7]. If the solid circulation rate exceeds this value, a high densidy circulating fluidized bed (HDCFB) should be considered. Moreover, a high solid circulation rate causes high pressure drop in the bed, high particle attrition and some operational problems. Therefore, it is better to operate the chemical-looping hydrogen generation system at ambient pressure.

The effect of solid circulation rate and steam velocity on the nickel-to-steam ratio and the equilibrium composition in the water splitting reaction at 900 °C and 1 atm is shown in Fig. 5. The solid circulation rate was varied in the range of 10-100 kg/m^{2}s (i.e., common solid circulation rate in the commercial circulating fluidized beds). The nickel-to-steam mole ratio increases with increasing solid circulation rate and decreasing steam velocity. The hydrogen yield increases as the solid circulation rate is increased and decreasing steam input velocity because the nickel-to-steam ratio increases with the solid circulation rate (Fig. 3). Consequently, higher solid circulation rate and lower steam velocity lead to higher nickel-to-steam mole ratio that leads to higher hydrogen yield. For example, Fig. 5(b) indicates that the hydrogen yield is 89% at 0.1 m/s of steam input velocity and 100 kg/m^{2}s of solid circulation rate.

The effect of syngas composition on the heat of reaction in the reduction reaction was determined. The main components of syngas from the gasification of heavy residue are CO, H_2, CO_2 and CH_4. When NiO is used as a metal component in the oxygen carrier particle, the reaction equations for the water splitting reaction and the reduction reaction are shown in Eqs. (7) to (10) and the heat of reaction was calculated based on the Hess law:

Water splitting:

$$Ni+H_2O \rightarrow NiO+H_2 \qquad (H_{900}=3.47\ \text{kcal/mol-}H_2O) \tag{7}$$

Reduction

$$4NiO+CH_4 \rightarrow CO_2+2H_2O+4Ni \qquad (H_{900}=32.40\ \text{kcal/mol-}CH_4) \tag{8}$$

$$NiO+H_2 \rightarrow H_2O+Ni \qquad (H_{900}=-3.47\ \text{kcal/mol-}H_2) \tag{9}$$

$$NiO+CO \rightarrow CO_2+Ni \qquad (H_{900}=-11.34\ \text{kcal/mol-CO}) \tag{10}$$

The water splitting reaction and the reduction of NiO by methane are endothermic, but the reduction by H_2 and CO is exothermic. The effect of syngas composition on the heat of reduction of syngas at 900 °C, 1 atm is in Fig. 6. The heat release increases as CO concentration is increased at a given CH_4 concentration. How-

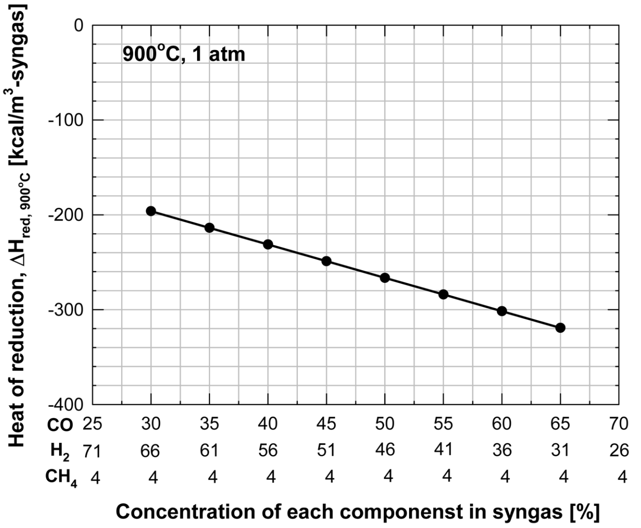

Fig. 6. Effect of the syngas composition on the heat of reduction at 900 °C.

ever, the heat release decreases as the CH_4 concentration is increased because CO and H_2 concentrations decrease. Consequently, higher CO concentraion and lower CH_4 concnetration are favorable to operate the reduction reactor without energy input. For example, syngas from gasification of the heavy residue in S company contains 2.1% CH_4, 41.0% CO, 46.6% H_2, and 10.3% CO_2. The heat of reduction is −249.3 kcal/m^3-syngas. Therefore, the reduction reaction is exothermic and the heat from the reduction reactor can be transported to the water splitting reactor by circulating solids and it can save energy requirements for endothermic reaction in the water splitting reactor.

PROCESS CONFIGURATION

The chemical-looping hydrogen generation system consists of two inter-connected reactors, the water splitting reactor and the reduction reactor. Moreover, the system requires a solid conveying system and a gas sealing between two reactors. The process configuration for chemical-looping hydrogen generation has to satisfy the following requirements: (1) high mass and heat transfer, (2) easy solid conveying between two reactors, (3) perfect gas sealing between two reactors, and (4) easy reaction control. To safisfy these requirements, numerous process configurations should be considered, but a fluidized bed system has been selected as the most promising reactor due to its advanteages of fluid-like behavior of solids in the reactor, high mass and energy transfer efficiency, and easy solid conveying. The possible configurations of the chemical-looping hydrogen generation system based on the fluidized bed reactors are shown in Fig. 7. The charateristics of each configuration are summarized in Table 1. As mentioned, higher solid circulation rate and lower steam input velocity are favorable for higher hydrogen yield. Moreover, low gas velocity in the reduction reactor is favorable for the reaction conversion. Therefore, bubbling fluidized beds are suitable for a water splitting reactor and a reduction reactor. For the high solid circulation rate, the system requires a transport bed for solid conveying between two reactors. Consequently, two bubbling beds for the water splitiing reactor and the reduction reactor and one transport bed for solid conveying are necessary for the chemical-looping hydrogen generation system. Finally, bubbling-bubbling-transport mode, as shown in Fig. 7(b), was selected as a suitable process configuration. However, if the attrition loss of oxygen carrier particle is too severe, bubbling-bubbling mode with gas switching, as shown in Fig. 7(c), can be considered as a suitable process configuration.

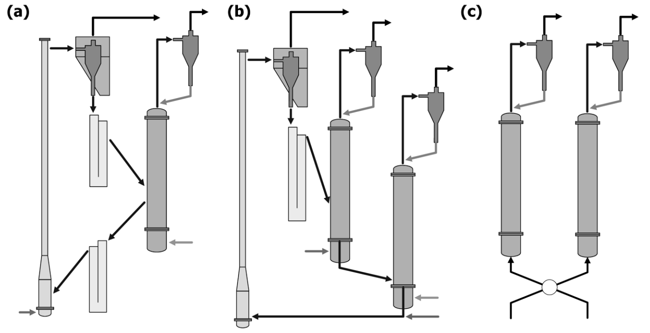

Fig. 7. Possible configurations of two interconnected fluidized bed system for the chemical-looping hydrogen generataion system, (a) transport-bubbling, (b) bubbling-bubbling-transport, (c) bubbling-bubbling.

CONCLUSIONS

To find a suitable metal component in oxygen carrier particles for a chemical-looping hydrogen generation system (CLH), oxygen transfer capacities of metal components were compared, and Ni was selected as the best metal component. The proper operating conditions to achieve high hydrogen generation rate have been determined based on the chemical-equilibrium composition analysis for a water splitting reactor. Higher solid circulation rate and lower steam input velocity lead to higher nickel-to-steam mole ratio that results in higher hydrogen yield. The suitable compositions of syngas from a gasifier of heavy residue to achieve high energy efficiency have been investigated by calculating the heat of reaction. Higher CO concentraion and lower CH_4 concentration are favorable to operating the reduction reactor without additional energy input. Based on the selected operating conditions, the best configu-

Table 1. Chracteristics of process configurations

Mode	Heat up/cool down of particle	Operation	Attrition loss of particle	Reactivity of particles	Fan power
a) T-B	Easy	Easy	High	Require high reaction rate in a transport bed	High
b) B-B-T	Easy	Very difficult	High	Available for low reaction rate	High
c) B-B	Difficult	Very easy	Very low	Available for low reaction rate	Low

ration of two interconnected fluidized beds system for the chemical-looping hydrogen generator has been devised. The bubbling-bubbling-transport mode was selected as the best process configuration.

ACKNOWLEDGMENT

This work was supported by Ministry of Commerce, Industry and Energy (MOCIE) and Korea Research Council of Public Science & Technology (KORP).

REFERENCES

1. R. Kothari, D. Buddhi and R. L. Sawhney, *Int. J. Global Energy Issues*, **21**, 154 (2004).
2. K. Hassmann and H. Kuhne, *Int. J. Hydrogen Energy*, **18**, 635 (1993).
3. IEA Report, *Prospects for hydrogen and fuel cells*, IEA Publications, PDF version (2005).
4. H. J. Ryu and G. T. Jin, *Korean Chem. Eng. Res.*, **42**, 588 (2004).
5. H. J. Ryu, D. H. Bae, K. H. Han, S. Y. Lee, G. T. Jin and J. H. Choi, *Korean J. Chem. Eng.*, **18**, 831 (2001).
6. H. J. Ryu, D. H. Bae and G. T. Jin, *Korean J. Chem. Eng.*, **20**, 960 (2003).
7. H. J. Ryu and G. T. Jin, *Energy Eng. J.*, **12**, 289 (2003).