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CHEMICAL-LOOPING STEAM METHANE REFORMING FOR HYDROGEN PRODUCTION IN A CIRCULATING FLUIDIZED BED REACTOR

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ABSTRACT

Two-step steam methane reforming for hydrogen production using a chemical looping system is proposed to improve the conventional processes. The reaction characteristics with iron oxides as an oxygen carrier was determined in a circulating fluidized bed reactor. From this system, high concentrated hydrogen can be continuously produced without any post treatment.

INTRODUCTION

Research activities on H₂ production are increasing rapidly since it is an environmentally sound fuel that does not emit carbon dioxide that is known to be one of the global warming gases. In particular, H₂ as a fuel for the mobile and stationary power generation by using fuel cell has a great potential to increase H₂ demand in the near future. Steam reforming of natural gas (i.e., mainly CH₄) is the most common and well developed technology for H₂ production at large scale. However, this conventional process has additional post treatments such as water-gas shift reaction (WGS) and pressure swing adsorption (PSA) to concentrate or separate H₂ so that the capital and operating costs would be high. In this respects, several research projects are underway to produce syngas and H₂ by the chemical looping (CL) to improve conventional SMR processes (1-3).

Chemical-looping steam methane reforming (CL-SMR) for H₂ production is a novel concept which can produce highly concentrated H₂ and CO₂ as the reaction products. The CL-SMR system consists of fuel reactor (FR) for CH₄ oxidation and steam reactor (SR) for steam reduction, where oxygen carriers (metal oxides)

circulate between the two reactors. Reactions of the CL-SMR are as follows;



where MO is fully oxidization state of metal oxides and M is metal or reduced metal oxides.

At present, studies on the CL-SMR for hydrogen production are limited to theoretical analysis of the materials and reactivity test of small amount of the samples. On the other hands, pilot-scale experimental study for mass production and interpretation of empirical data are relatively sparse. To operate stable solid circulation and maintain the good reaction condition in a fluidized bed reactor, the hydrodynamic characteristics in the CL-SMR system (solid circulation rate, prediction of solid circulation rate at high temperature, gas leakage between reactors, and steady state operation) have been determined in this study. Also, the optimum operating conditions and the reactor performance in the continuous operation were determined.

EXPERIMENTAL

Oxygen-carrier

For the redox reaction, about 13 wt% reduced iron (45-125 μm , average 85 μm , Junsei Chemical. Co. Ltd) as a raw material of the oxygen carrier and zirconia-silica beads (63-120 μm , average 95 μm) as a thermal medium were used in this study. Before the experiment, the raw materials were mixed physically in the bed and then were fully oxidized with steam at 1073K for about 5 h. Afterwards, the solid particles were sampled to determine weight fraction of the iron oxides (Fe_3O_4). From the thermo-gravimetric analysis, weight fraction of Fe_3O_4 was 17% in the bed. Total inventory of solids in the bed was 13.3 kg.

Circulating fluidized bed reactor system

Schematic diagram of the CL-SMR reactor with their dimension is shown in Fig. 1. It consists of two bubbling fluidized bed reactors for methane oxidation (Fuel Reactor, FR) and steam reduction (Steam Reactor, SR), a non-mechanical L-valve for regulating the solid circulation rate through the two beds, and a riser for solid recirculation

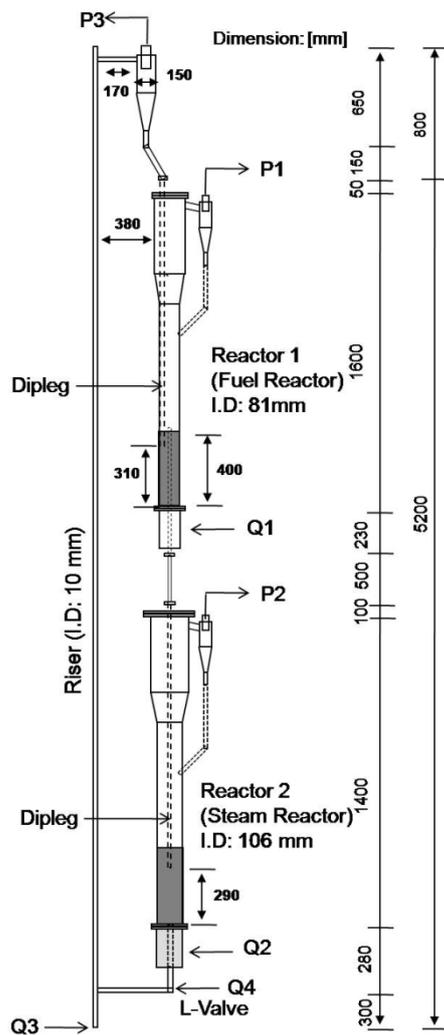


Figure 1. Schematic diagram of CL-SMR system (Q: gas inlet, P: gas outlet)

In Fig. 1, Q1, Q2, Q3, and Q4 are gas inlet of CH₄, steam, N₂ (for transportation), N₂ (for controlling the solid circulation rate), respectively, and P1, P2, P3 represent the product gas outlet. The reactor made of stainless steel (SUS 304) pipe and it was heated with electric Kantal wires and insulated with ceramic fiber wool to prevent heat loss to surroundings. Bubble-cap type distributor plates were installed at the bottom of FR and SR reactors for uniform gas distribution. To prevent gas mixing between two reactors during solid circulation, dipleg pipes were installed in the each bed. To measure pressures in the bubbling beds and the riser, pressure transmitters (Sensys) were installed in each section. All the obtained data of pressure and temperature in the bed were stored in a computer using data logger (Midi Logger, Graphtec Co. Ltd). The exit gases from the reactors were passing through a condenser to remove water vapor and then sent to the gas analyzer. The on-line analyzers determine the components of CO, CO₂ and CH₄ by using an IR measurement (Fuji. Co. Ltd). The hydrogen was analyzed by using on-line TCD detector.

RESULTS AND DISCUSSION

Hydrodynamic study

For the hydrodynamic study, zirconia-silica beads were used and moisture was removed at the reactor temperature of 423K. Inert N₂ gas was used as the fluidizing gas this experiment.

Minimum fluidization gas velocity and transitional gas velocity

The minimum fluidizing gas velocity of the solid particle is determined to be 0.016

m/s which are similar to the predicted value of 0.013 m/s from the correlation of Wen and Yu (4). Transitional gas velocity which is the boundary between the turbulent and fast fluidization regimes is determined to be 2.0 m/s by the emptying time method (Bae et al., 5).

Solid circulation rate measurement

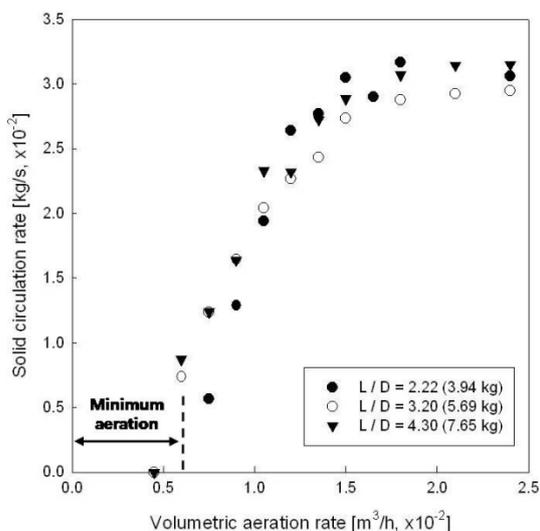


Figure 2. Effect of aeration rate in the L-valve and the bed height to diameter (L/D) ratio on solid circulation rates

through the particles and then through the constricting bend of L-valve. However, a local large void is formed and stagnates near the aeration point beyond a certain aeration rate and the solid circulation rate becomes almost constant above that aeration rate. Conceivably, the rising void velocity may equal that of the bulk down-flow of solids (Zenz, 7).

Correlation of solid circulation rate with pressure drop in the riser

Direct methods to measure solid circulation rate in hot units are not generally available due to the sealing problem and selection of reactor materials at high temperature. Therefore, the alternative method to correlate solid circulation rate with differential pressure in the bed is proposed by Dry et al. (8). In particular, differential pressure in the riser would be a best way to determine solid circulation rate since it

As can be seen in Fig. 2, solid flow commences beyond 0.6 m³/h. This is well agreed with the fact that L-valve and loop-seal have a certain minimum gas flow rate to operate (Yang and Knowlton, 6). Afterwards, solid flow increases linearly with the aeration rate in L-valve and then exhibits a maximum value around 0.03-0.032 kg/s. It is independent from the variation of bed inventory at the given operating condition. When the aeration gas is injected into the L-

valve, it lubricates the packed solids to facilitate their movement in the vertical section of L-valve. The aeration gas moves downwards

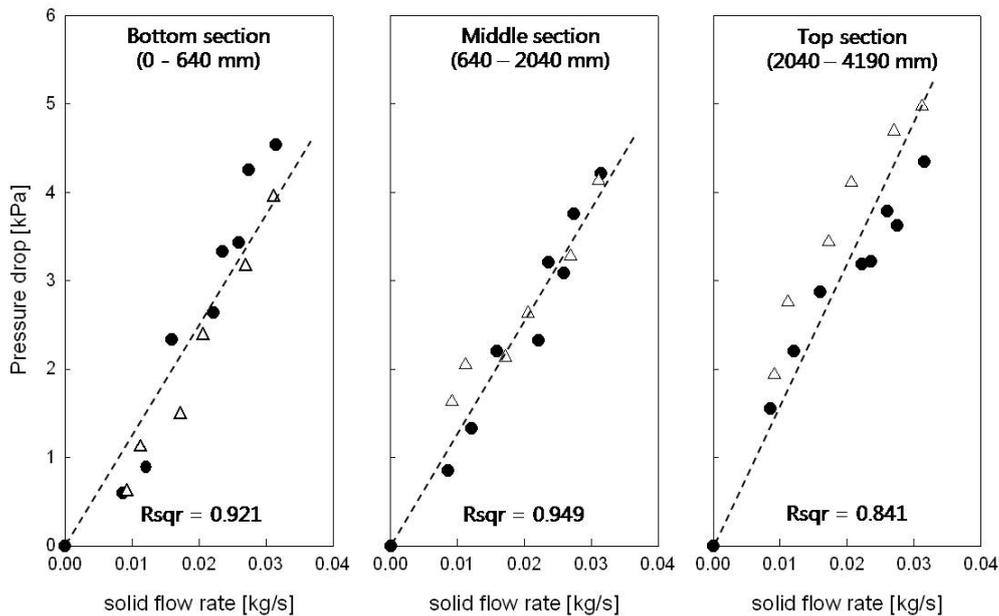


Figure 3. ΔP change with variation of solid flow rate and gas velocity in the riser at different position of riser (●: 5.30 m/s, △: 6.36 m/s)

mainly depends on solid weight regardless of the system conditions. If this approach is used, it is necessary to determine the strongest correlation with solid circulation rate with differential pressure in the different sections of the riser. As can be seen in Fig. 3, solid flow rate and differential pressure in the CL-SMR system exhibit linear relationship in the middle section of the riser. Therefore, the solid flow rate can be correlated with pressure drop in the hot unit as shown in Eq. 3. In the top section of the riser, however, the regression coefficient is shown to be the lowest and the effect of gas velocity on ΔP is also significant in this section due to the exit effect caused by the riser geometry where the gas flow in the top section has a larger restriction than the other sections due to solids' refluxing at the right angle outlet of the riser.

$$\Delta P \text{ [kPa]} = 127.8 F_s \text{ [kg/s]} \quad (3)$$

Redox reaction study

Effect of reaction temperature on methane oxidation in FR

Methane conversion by oxidation with variation of temperature is shown in Fig. 4. In this experiment, CH_4 concentration to the FR was maintained at 20% and steam was supplied twice of the stoichiometric value. The solids circulation rate was

maintained high enough to give oxygen needed for CH₄ oxidation during the operation. As can be seen, the reaction starts from around 1040 K and the reaction conversion increases with temperature - since the reaction is endothermic nature. The product gas composition is also a function of reaction temperature. As can be

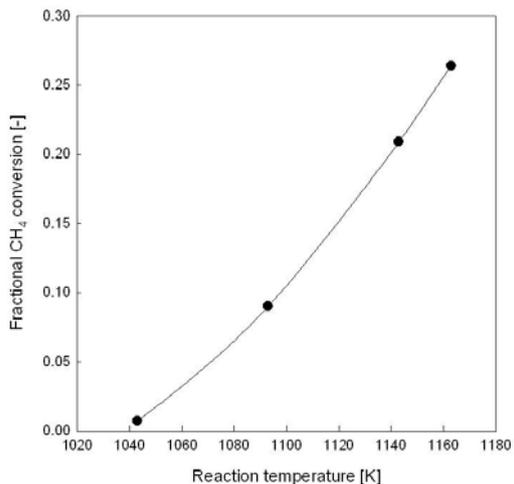


Figure 4. Fractional CH₄ conversion with variation of reaction temperature at FR ($U_{FR} = 0.0408$ m/s, Temp. at SR: 1173 K)

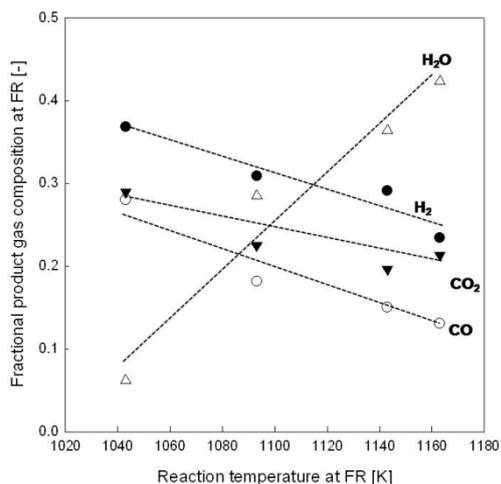


Figure 5. Fractional product gas composition with variation of reaction temperature at FR ($U_{FR} = 0.0408$ m/s, Temp. at SR: 1173 K)

seen in Fig. 5, concentrations of H₂, CO, and CO₂ decrease and concentration of H₂O increases with increasing temperature. The product gas compositions agree with the equilibrium composition. In the experimental data, there are no by-product such as CO, CO₂, and CH₄ in SR due to carbon deposition in FR.

Effect of solid circulation rate on methane oxidation in FR

At the steady state operation of the CL-SMR system, oxygen carriers play an important role in oxygen transfer between FR and SR, where the amount of oxygen with the stoichiometric ratio to the amount of fuel (CH₄) was supplied. This oxygen to fuel ratio is defined based on the reaction stoichiometry of CH₄ oxidation and a corresponding value to the oxygen carrier for complete CH₄ conversion. The effect of solid circulation rate on CH₄ oxidation at 1173K and $2.5u_o/u_{mf}$ is shown in Figs. 6 and 7. In Fig. 6, CH₄ conversion increases with solid circulation rate and then converges to 42% at solid circulation rate over 0.008 kg/s. At this condition, the theoretically required solid circulation rate corresponds to 0.0048 kg/s (O/F = 1) which is lower than that obtained from the experiment. In other words, O/F ratio should be maintained about 1.67 times as much as the theoretical value in the

practical CL-SMR system for the steady state operation. The effect of solid circulation rate on the product gas composition from CH_4 oxidation is shown in Fig. 7. When the O/F ratio is below unity, it can be known that partial oxidation of CH_4 is favored (H_2 and CO increases while H_2O and CO_2 decreases).

Cyclic redox reaction of CL-SMR system

The system temperature and bed pressure were monitored in the number of redox cycles to maintain the steady state operation at 1173 K. During 20 redox cycles, both reaction temperature and pressure remained constant and stable solid circulation was maintained at the constant pressure drop in the riser (in the middle section). At this condition, CH_4 of 0.025 mol/min and steam of 0.125 mol/min was supplied into FR and SR, respectively. It is found that approximately steam (31%), H_2 (18%), CO (7.5%) and CO_2 (10%), and the unconverted CH_4 were continuously obtained from the FR. Based on the volume change of gas inside the reactor, CH_4 conversion is around 42%. Meanwhile, 14% of H_2 and the un-reacted steam were detected in the SR. There was no CO_x product due to carbon deposition from FR.

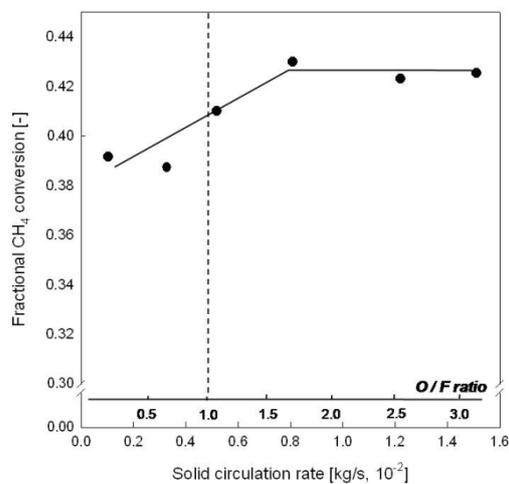


Figure 6. Fractional CH_4 conversion as a function of solid circulation rate at FR ($U_{\text{FR}} = 0.0340$ m/s, Temp. at FR: 1173 K)

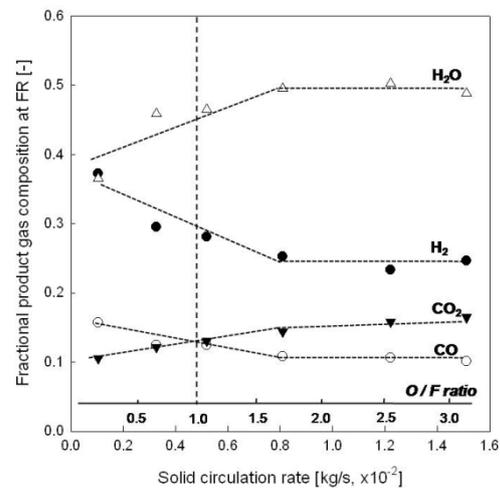


Figure 7. Fractional product gas composition with variation of solid circulation rate at FR ($U_{\text{FR}} = 0.0340$ m/s, Temp. at FR: 1173 K)

CONCLUSIONS

Solid circulation rate increases with increasing aeration rate in the L-valve up to 0.032 kg/s and it is independent from the variation of bed inventory. The solid circulation rate is correlated with pressure drop in the middle section of the riser. Gas leakage between two reactors can be prevented by installing a dipleg pipe into the each bed. The cyclic redox reaction was performed over 20 times at the given reaction temperature and pressure. During the operation, 38 L/h hydrogen (12 L/h from FR and 26 L/h from SR) can be obtained and it corresponds to 1.04 mol of H₂ production per one mol of CH₄ supply. In particular, the produced hydrogen from the SR is pure without any CO_x contamination.

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