Improved Reduction of Carbon Monoxide by Highly Efficient Catalytic Shift for Fuel Cell Applications

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Abstract

The generation of high purity hydrogen from reformed hydrocarbon fuels, or syngas, is essential for efficient operation of the fuel cell (PEMFC, Polymer Electrolyte Membrane Fuel Cell). Usually, major components of reformed gas are H_2, CO, CO_2 and H_2O. Especially a major component, CO poisons the electrode of fuel cells. The water gas shifter (WGS) that shifts CO to CO_2 and simultaneously produces H_2, was developed to a two stage catalytic conversion process involving a high temperature shifter (HTS) and a low temperature shifter (LTS). Also, experiments were carried out to reduce the carbon monoxide up to 3~4% in the HTS and lower than 5,000 ppm via the LTS.

Keywords: Hydrogen, Carbon monoxide, WGS, HTS, LTS

1. Introduction

Fuel cells promise to be an efficient and clean alternative to fuel combustion for primary power generation of stationary and mobile source applications in the near future.[1,2] They are about twice as fuel efficient as the internal combustion engine, they do not produce virtually CO, HC or NO_x and they reduce the level of CO_2. Representative techniques for producing hydrogen using natural gas include steam reforming, partial oxidation reforming, and auto-thermal reforming.[3-5] Particularly, the production gas in the partial oxidation reforming contains about 10~20% carbon monoxide, compared to other reforming method. And since the high carbon monoxide concentration causes electrode poisoning of fuel cells, carbon monoxide concentration in reforming gas must be maintained at lower than 10 ppm.[6]

In general, shift reactions consist of the high temperature shifter (HTS) reaction and low temperature shifter (LTS) reaction. The HTS reaction has an operating temperature of 350~450°C and reduces carbon monoxide concentration to 3~4%. The LTS reaction that is operated between 200~250°C and reduces carbon monoxide concentration to lower than 0.5%.[7]

Some studies on shift reactions that have been carried out include research on the activation of shift reactions using a catalyst for reducing carbon monoxide,[8] research on a compact na-

tural gas reforming system,[9,10] and development of hydrogen production equipment for fuel cells.[11,12] Even though the parameters that affect shift reaction such as reaction temperature, space velocity, and ratio of steam and dry gas are included in these papers, more detailed studies are needed.

The shift reaction is an important unit process for reducing carbon monoxide in the reforming gas. Recently, studies on producing hydrogen for compact type fuel cells have been effectively achieved. Studies on shift reaction have been focused on catalyst activation. However, detailed data for operation is insufficient. Therefore, there is a need for a study on the operating conditions and characteristics of the shift reaction.

In this study, reactors for HTS and LTS were designed and manufactured in order to reduce carbon monoxide concentration in the resulting reforming gas to lower than 0.5%. In order to reduce carbon monoxide concentration to 3~4% in the HTS reactor, experiments were carried out to measure changes in carbon monoxide and hydrogen concentration with respect to change in shift reaction affecting the parameters. By changing the LTS reaction to affect parameters such as steam flow rate and space velocity, carbon monoxide concentration was reduced to lower than 0.5% and the optimum operating condition was obtained.

2. Experimental Equipment and Methods

Fig. 1 shows the experiment equipment used for the reforming gas shift reaction. It consists of a gas supply line, a steam supply

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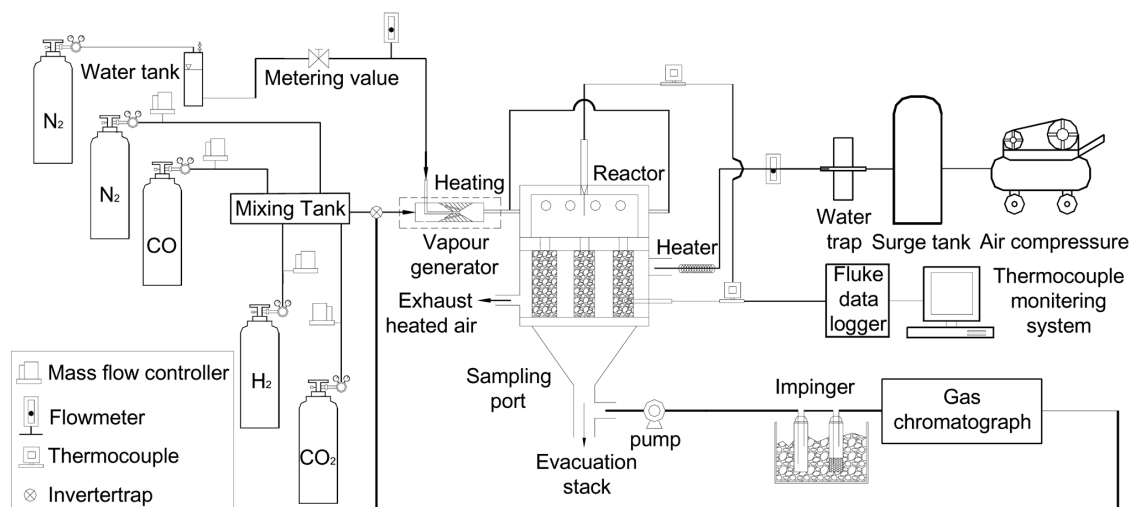Tel: +82-62-230-7156, Fax: +82-62-230-7156

Fig. 1. Schematic diagram of the water gas shift.

line, reactors for the HTS and the LTS, an air supply line, heat exchanger, and analysis line. The flow of hydrogen, carbon monoxide, carbon dioxide, and nitrogen are controlled precisely, mixed in a mixture tank and then supplied through the gas supply line at each MFC (Bronkhorst, F201AC-FAC-22-V, Netherlands). The flow of distilled water supplied from the water tank is controlled using a flow quantity meter and a metering valve. It is combined with simulated gas in the carburetor. The resulting, completely vaporized compound, is inserted in the reactor through the steam supply line. To obtain a uniform catalyst temperature distribution, the reactors for the HTS and the LTS were designed and manufactured using the heat exchanger of a coaxial rectangular tube type. Fe based catalyst (Süd-Chemie, G-3C, Germany) which is used for reaction temperature range of 300~500°C was put into the HTS reactor. For the LTS reaction, a Cu-Zn based catalyst (Süd-Chemie, C18, Germany) between 195~230°C was used. To adjust the reaction temperature, a K-type thermocouple was installed within the reactor and measurements were taken using a Data Logger (Fluke, 2625A Data logger, USA). Air is compressed, stored in the air tank where moisture is eliminated, heated to a uniform temperature and supplied to the double pipe of the reactor via the air supply line. Experiments were then carried out for HTS and LTS, respectively. The analysis line consists of a sampling line and a gas chromatograph (SHIMADZU, GC-14B, Japan).

The standard conditions for each variable obtained in the HTS and the LTS are shown in Table 1, the optimum experimental conditions and results obtained for each variable are shown in Table 2.

For both HTS and LTS reactor, emission gas was extracted from the sampling port installed at the reactor exit. Moisture was removed from the extracted samples by a cooling device and the resulting dry gas was inserted in the sampling loop of a gas chromatograph for analysis. A TCD detector was used in the analysis. For the analysis column, Molecular Sieve 5A (80/100 mesh) was used for hydrogen, Molecular Sieve 13X (80/100 mesh) was used for carbon monoxide, and HayeSep R (100/120 mesh) was used for carbon dioxide.

3. Results and Discussion

The reaction of carbon monoxide with water molecule produces carbon dioxide and hydrogen, as illustrated in formula (1).

$$CO+H_2O \rightarrow CO_2+H_2 \quad \Delta H = -41kJ/mol \quad (1)$$
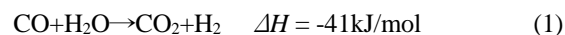
Since this reaction is exothermic, the equilibrium constant decreases with the increase in temperature. Therefore, the low temperature reaction is advantageous for obtaining a high conversion rate and it is not influenced by pressure. The HTS and

Table 1. Experiment conditions for the water gas shift

Conditions	Gas flow rate (L/min)	Components ratio (L/min)	Steam flow rate (L/min)	Temperature (°C)
Value (HTS)	8~16	1~4	4~13	300~500
Conditions	Space velocity (L/g h)	CO concentration (%)	Steam flow rate (L/min)	Temperature (°C)
Value (LTS)	2.8~5	4.0	1.2~5.6	195~230

Table 2. Experiment data for standard condition of the water gas shift

Variable	Flow rate (L/min)	Temperature (°C)	Steam (L/min)	H_2 concentration (%)	CO concentration (%)	CO conversion (%)
Value (HTS)	13	400	8	39.4	2.4	84.4
Variable	Space velocity (L/g h)	Temperature (°C)	Steam/gas	H_2 concentration (%)	CO concentration (%)	CO_2 concentration (%)
Value (LTS)	3.0	195~230	0.3	43.3	0.32	13.0

LTS reactions are used as a general method to reduce these thermo dynamic limitations. The main purpose of the HTS reaction is to increase the reaction speed and the LTS reaction is used to obtain a high conversion rate.

In this study, experiments were carried out to find the optimum operating condition for the HTS and the LTS reactions in order to reduce the amount of carbon monoxide which poisons fuel cell electrodes in the reforming gas stage to a level lower than 5,000 ppm.

3.1. Steam Flow Rate

In the reforming gas shift reaction, the conversion rate of carbon monoxide varies with the amount of steam flow rate. This effect is illustrated in Fig. 2.

In Fig. 2(a), the amount of simulated reforming gas inserted to the HTS entrance is 13 L/min, the ratio for $H_2 : CO : N_2$ is 3 : 2 : 5, and the steam flow rate varies within the range of 4~13 L/min. The carbon monoxide concentration decreased as the amount of steam increased while the amount of hydrogen actually increased. However, if steam flow rate exceeds 4.6 L/min, that is, if the ratio of steam/gas is greater than 0.35, it is possible to reduce the final carbon monoxide concentration at the reactor to a level lower than 4%. However the change is not large from the point as the steam input goes over 8 L/min, that is, if the steam/gas ratio is greater than 0.6. When carburetor load and concentration reduction rate of carbon monoxide were taken into account, the highest efficiency was obtained when the steam/gas ratio was 0.6.

For the LTS catalyst, the change in hydrogen and carbon monoxide concentration caused by change in steam flow rate is shown in Fig. 2(b). The simulated gas emitted by the HTS reactor is 13 L/min, the ratio of $H_2 : CO : CO_2 : N_2$ is 40 : 4 : 6 : 50, and the range of change for steam flow rate is 1.2~5.6 L/min. As shown in Fig. 2(b), when steam flow rate is higher than 4 L/min, that is, when the steam/gas ratio exceeds 0.3, the final carbon monoxide concentration at the entrance of the reactor was re-

duced to 5,000 ppm. When carburetor load and concentration reduction rate of carbon monoxide were considered, the highest efficiency was obtained when the ratio of steam/gas was 0.3.

3.2. Reforming Gas Component

In this experiment H_2/CO ratio was varied to improve carbon monoxide reduction performance for the HTS reactor and the resulting carbon monoxide concentration is shown in Fig. 3. The $H_2 : CO : CO_2 : N_2$ ratio for the LTS reaction was constant. In Fig. 4, of the 13 L/min simulated reforming gas flow rate, 50% is N_2. Carbon monoxide concentration was obtained by changing H_2/CO ratio within the range of 1~4. As H_2/CO ratio increased, carbon monoxide concentration decreased proportionally and hydrogen concentration increased. As the H_2/CO ratio increased by over 2, the carbon monoxide concentration showed a reduction.

3.3. Reactor Temperature

An experiment to assess the impact of changing the catalyst temperature was carried out to observe the basic activation for the commercial catalyst used in the HTS reaction for reforming gas. Change in hydrogen and carbon monoxide concentration was explored by varying the temperature within the range of 300~500°C, the operating range of the catalyst temperature for the HTS reaction. For the LTS catalyst, operating temperature was kept constant at 195~230°C. This was done to obtain basic experimental data to predict the performance when the commercial catalyst is applied to compact system.

In this study, a simulated reforming gas flow rate of 13 L/min, a gas component ratio of $H_2 : CO : N_2$ is 3 : 2 : 5, and a steam and simulated reforming gas ratio of 0.5 was used. Carbon monoxide and hydrogen were analyzed at catalyst temperature range of 300~500°C using the HTS reactor. These results are shown in Fig. 4. Carbon monoxide concentration decreased as temperature was increased and carbon monoxide conversion
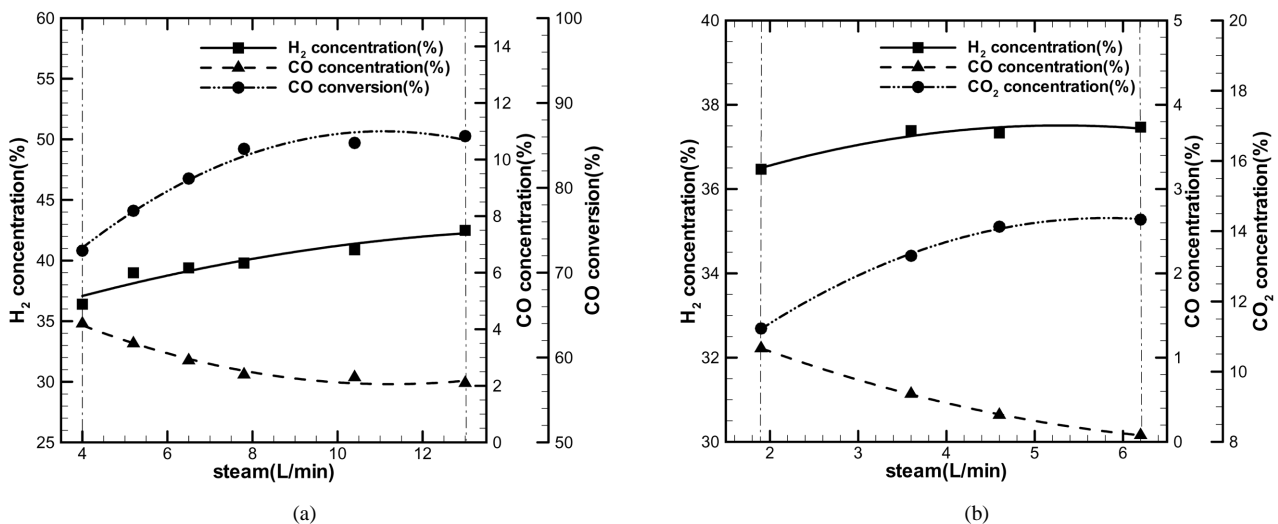

Fig. 2. Composition change as a function of steam in (a) the high temperature shift and (b) the low temperature shift.
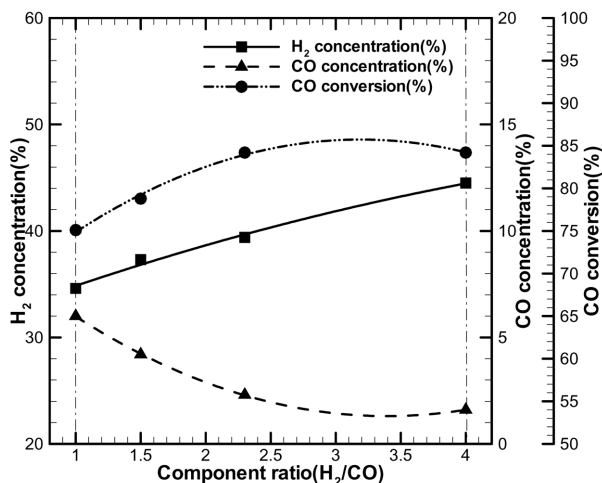
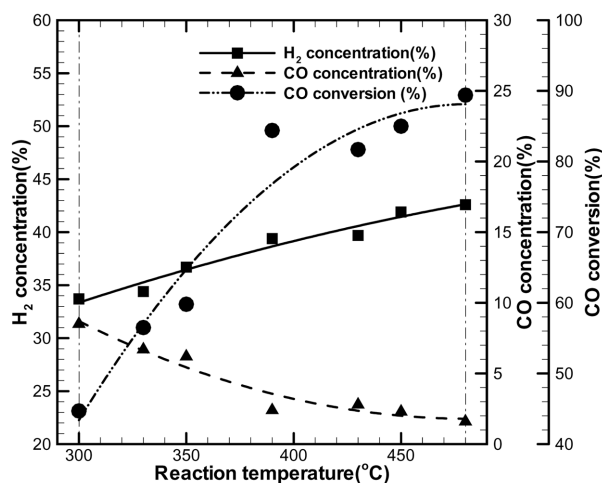Fig. 3. Effect of gas component ratio in the HTS.

Fig. 4. Equilibrium concentrations for the HTS as a function of temperature.

rate also increased.

However, in order to reduce carbon monoxide concentration lower than 4% for the HTS, the catalyst reaction temperature must be maintained over 370°C. In addition, while hydrogen concentration increased with temperature, the change was not large for temperatures exceeding about 400°C. For the HTS, when carbon monoxide concentration was reduced lower than 4%, the optimum hydrogen concentration and heat efficiency were approximately 400°C.

3.4. Reforming Gas Flow Rate

In order to find out the efficiency for the reactor of reforming gas shift, equipment for HTS and LTS were designed and manufactured and the carbon monoxide concentration change caused by changing the reforming gas flow rate, or space velocity, was analyzed. Change in the carbon monoxide and H_2 concentrations caused by changing the reforming gas low rate in the HTS reactor is shown in Fig. 5(a). In Fig. 5(a), the concentration of car-

bon monoxide and hydrogen increased when reforming gas flow rate was changed by 8~16 L/min. However, carbon monoxide concentration was maintained at lower than 4%.

The relationship between space velocity and hydrogen concentration vs. carbon monoxide concentration in the LTS reactor is shown in Fig. 5(b). In Fig. 5(b), when space velocity of the simulated reforming gas emitted from the HTS was changed within the range of 2.8~5 L/(g h) the carbon dioxide concentration increased along with the carbon monoxide concentration. In Fig. 5(b), when space velocity reached lower than 3 L/(g h), carbon monoxide concentration was reduced lower than 5,000 ppm.

4. Conclusion

HTS and LTS reactors were proposed to reduce carbon monoxide concentration which is harmful at catalyst electrodes in a fuel cell stack.

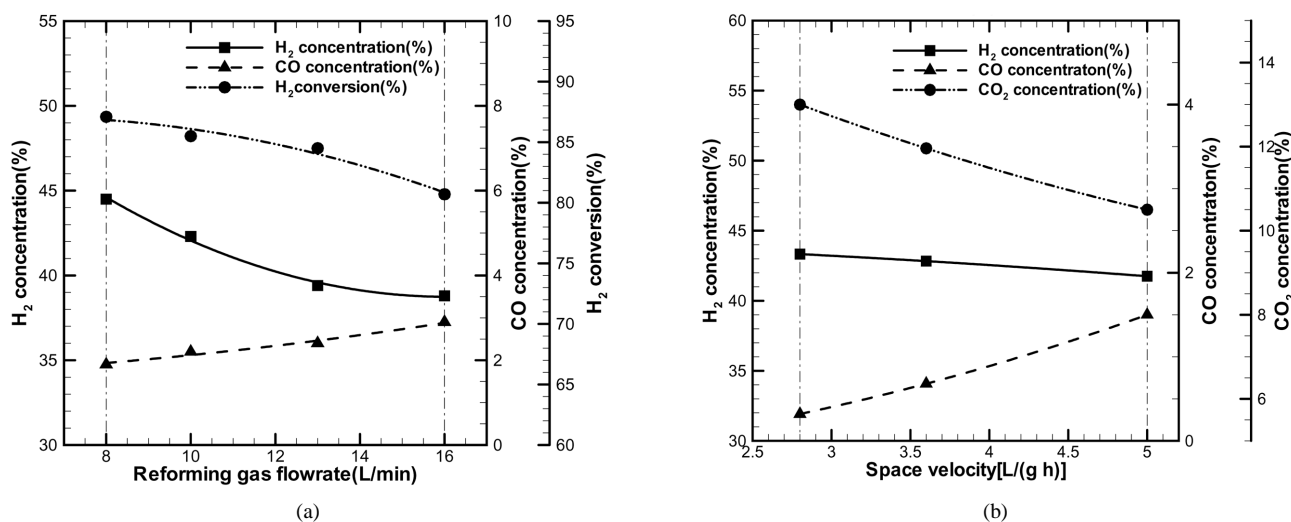The experiments were carried out about steam flow rate, refor-

(a)

(b)

Fig. 5. Composition change as a function of space velocity in (a) the high temperature shift and (b) the low temperature shift.

ming gas component, reactor temperature, and reforming gas flow rate. The results are as follows;

1) The highest efficiency of HTS was optimized when the steam/gas ratio was 0.6. It is possible to reduce the final carbon monoxide concentration to a level lower than 4%. Also, the LTS was optimized when the steam/gas ratio was 0.3. At that time, the final carbon monoxide concentration was confirmed to a level lower than 5,000 ppm.

2) As the H_2/CO ratio increased by over 2, the carbon monoxide concentration was confirmed to a level lower than 4% at the HTS.

3) When the optimum hydrogen concentration and heat efficiency were about 400°C, carbon monoxide concentration was reduced to a level lower than 4%.

4) In HTS, when reforming gas flow rate was changed within 8~16 L/min, carbon monoxide concentration was maintained to a level lower than 4%. Also, when space velocity reached lower than 3 L/(g h), carbon monoxide concentration was reduced to a level lower than 5,000 ppm.

Acknowledgements

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