Short communication

Design of an integrated fuel processor for residential PEMFCs applications

Yu Taek Seo [a], Dong Joo Seo [a], Jin Hyeok Jeong [b], Wang Lai Yoon [a],*

[a] *Hydrogen and Fuel Cell Research Department, Korea Institute of Energy Research (KIER), 71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea*
[b] *Chemical Engineering Department, Kyungpook National University, Republic of Korea*

Abstract

KIER has been developing a novel fuel processing system to provide hydrogen rich gas to residential PEMFCs system. For the effective design of a compact hydrogen production system, each unit process for steam reforming and water gas shift, has a steam generator and internal heat exchangers which are thermally and physically integrated into a single packaged hardware system. The newly designed fuel processor (prototype II) showed a thermal efficiency of 78% as a HHV basis with methane conversion of 89%. The preferential oxidation unit with two staged cascade reactors, reduces, the CO concentration to below 10 ppm without complicated temperature control hardware, which is the prerequisite CO limit for the PEMFC stack. After we achieve the initial performance of the fuel processor, partial load operation was carried out to test the performance and reliability of the fuel processor at various loads. The stability of the fuel processor was also demonstrated for three successive days with a stable composition of product gas and thermal efficiency. The CO concentration remained below 10 ppm during the test period and confirmed the stable performance of the two-stage PrOx reactors.
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Keywords: Fuel processor; Natural gas; Steam reforming; Residential co-generation; Polymer electrolyte fuel cell

1. Introduction

KIER has been conducting research and development on fuel cells, hydrogen production, and storage with an emphasis on polymer electrolyte membrane fuel cell (PEMFCs) powered systems and distributed hydrogen production systems from natural gas or renewable sources. A PEMFC-based cogeneration system for residential use has been considered to be suitable for small scale distributed power, which involves a PEMFC stack with a hydrogen generation system to provide hot water and electricity to one family household. High efficiency, low noise, and low emission of air pollutants should be the major benefits obtained from the use of PEMFC system [1]. Because of the limited existing hydrogen infrastructure, small scale hydrogen generation systems are needed to find an economical technology for producing hydrogen. While water electrolysis coupled

with commercial grid or renewable energy sources still need to reduce the hydrogen production cost, the hydrogen production cost from distributed natural gas is known to approach to the cost goal of being competitive with the cost of gasoline in 2015 [2]. Moreover there exist well developed natural gas infrastructures in Korea, in which natural gas pipelines are connected to most families and provides hot water for heating. Accordingly, the hydrogen rich reformate from natural gas is suitable for residential PEMFC systems in terms of infrastructure and technical abundance. Many types of fuel processing system are being developed to produce hydrogen that is pure enough and fast enough to supply to PEMFCs [3–5]. Although the steam reforming process needs more start up time than an autothermal reforming process, it provides hydrogen concentrations above 75% in a dry product gas, while the autothermal reforming process gas contains less than 50% of hydrogen because of the high nitrogen content that is supplied for internal combustion of natural gas and air [6]. Therefore a natural gas fuel processor adopting steam reforming has been developed in KIER as one of the key components for a residential PEMFC system. During

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* Corresponding author. Tel.: +82 42 860 3070; fax: +82 42 860 3309.
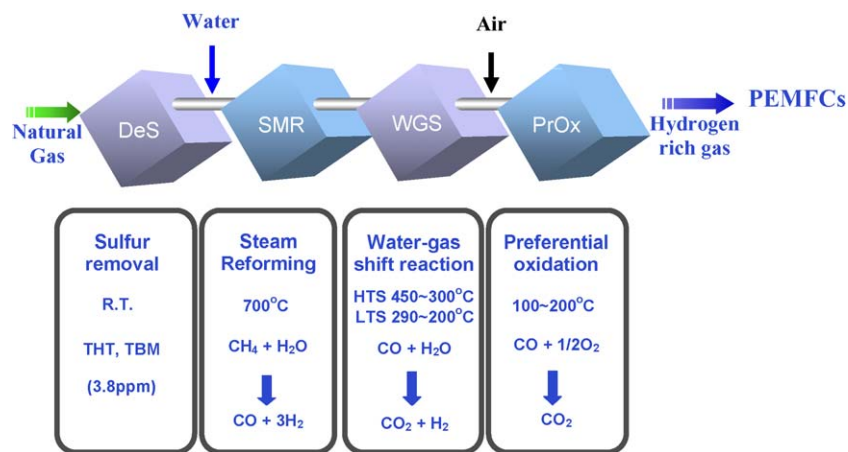*E-mail address:* wlyoon@kier.re.kr (W.L. Yoon).

Fig. 1. Schematic diagram of unit processes of a fuel processing system.

FY 2005, KIER focused on developing compact integrated fuel processing systems with high efficiency and evaluated a prototype fuel processor. The unit processes are: natural gas steam reformer, water gas shift reactors, steam generator and internal heat exchangers, which are integrated into a single modular unit. Complete CO removal was achieved with a two-stage preferential oxidation (PrOx) process, connected to the integrated fuel processor separately due to its temperature control unit and air mixing devices which should induce a complex design for the fuel processor and increase of the production cost. The optimization of total added air made easy by temperature control and avoids excess air injection that causes unnecessary consumption of hydrogen by oxidation. Laboratory testing has been performed in order to investigate the steady state behavior at nominal load operation and also at partial load operation. In this paper, the fuel processor performance such as product gas composition and thermal efficiency is presented to demonstrate the performance of fuel processor.

2. Experiments

The fuel processing system is designed to produce hydrogen that provide an electrical power output of 2 kW for prototype I and 1 kW for prototype II. Steam reforming has been selected as the primary reforming technology, and the endothermic reaction heat is provided by an external burner to achieve a methane conversion of more than 85%. The principal design of the fuel processor is explained in Fig. 1, where the unit processes are schematically shown. Korean town gas was used as a fuel gas in order to evaluate the fuel processor under actual operating conditions for a Korean household. The composition of the city gas was 90.2 vol.% CH_4, 6.6 vol.% C_2H_6, 2.3 vol.% C_3H_8 and 0.9 vol.% C_4H_{10} with 3.8 ppm of sulfur compounds as odorants. The THT and TBM as odorants are desulfurized in a bed of Mn-based adsorbent at room temperature before introducing for the reforming process. After preheating the water to near boiling temperature in the steam generator using the exothermic heat of the water gas shift process, the steam and desulfurized natural gas are mixed and introduced into the steam reforming process. The hydrocarbon compounds of natural gas are

converted to H_2, CO, CO_2, and residual CH_4 on a Ru-based catalyst at about 700 °C. The reformed gases from the steam reforming process pass through two consecutive processes of high and low temperature water gas shift reaction at 400 °C and 250 °C, respectively. The Fe-based catalyst reduces the CO concentration to 3–5 vol.% with a high shift reaction rate and the CO concentration is reduced to below 1.0 vol.% by a Pt-based catalyst, which is known to have high performance in the shift reaction. By combining Fe- and a Pt-based catalyst, it is possible to reduce the CO concentration below 1.0 vol.% without use of an excessive amount of the Pt-based catalyst. The exothermic heat of the shift reaction is used to preheat the steam and natural gas mixture to 500 °C with the aid of combustion flue gas. Air added to the outlet gas from shift processes and the mixed gas is provided to the PrOx process. The oxidation of residual CO by O_2 reduces the CO concentration in the reformed gas to below 10 ppm, which is needed to avoid the poisoning of the anode catalyst of PEMFCs [7]. The two-stage PrOx reactors are adopted for the CO removal process because the amount of air added to reactor can be reduced by optimizing the additive air at each stage [8], and less exothermic heat is expected, resulting in easier temperature control of the catalyst beds. The Pt-based catalyst is used for the first stage and the Ru-based catalyst is used for the second stage.

The integrated fuel processor is composed of steam reformer, water gas shift reactors, steam generator, and internal heat exchangers in order to simplify the system configuration. The appearance of the integrated fuel processor with thermal insulation is shown in Fig. 2. The two-stage PrOx reactors are connected to the outlet of the water gas shift reactors and the temperature control unit is deployed only in the first PrOx reactor since the less exothermic reaction heat of second PrOx reactor can be easily removed without aid of the temperature control unit.

The test of the fuel the processor with load fluctuations is carried out with automatic control of the flow rates. Natural gas for the external burner and the steam reforming process was provided with mass flow controllers (Alicat Scientific), and air for the external burner and the PrOx processes was also provided with mass flow controllers (Alicat Scientific). The water

gas chromatograph (HP 6890N system, Agilent Technologies Inc.) equipped with a TCD, methanizer and FID using 8 vol.% H_2/He as carrier gas. The detection limit of CO is 5 ppm. The CO concentration in the reformed gas was also measured by an infrared gas analyzer for the CO concentration.

3. Results and discussion

Table 1 shows the performance of the prototype I and prototype II fuel processors at nominal load operations. Prototype I is designed to produce $2.0 \, Nm^3 \, h^{-1}$ hydrogen under the operation condition of S/C = 2.5 and $[O_2]/[CO] = 1.5$. The composition of the reformed gas at the outlet of the two-stage PrOx reactors was 71.4 vol.% H_2, 19.2 vol.% CO_2, < 10 ppm CO, 4.3 vol.% CH_4 leading the methane conversion of 81%. The thermal efficiency of the fuel processor is defined as the heating value of the produced hydrogen referred to the heating value of produced hydrogen for the reforming process and external burner, which is suitable to evaluate and characterize the stand-alone fuel processing system without recirculation of the anode off gas [10,11]

$$\eta = \frac{\Delta H_{H_2\text{-HHV}} n_{H_2}}{\Delta H_{NG\text{-HHV}}(n_{NG\text{-reforming}} + n_{NG\text{-burner}})}$$

Prototype I shows a thermal efficiency of 73% on the higher heating value (HHV) basis. After confirming the initial performance of prototype I, it was coupled with a PEMFC single cell to test the durability at nominal load operation. The CO concentration in the product gas was below 10 ppm during the 3 day operation and the hydrogen concentration was stable as shown by no failure to producing electricity in the PEMFC single cell. The overall results are shown in our previous report [12].

The development of prototype I provides much information on how to improve the design and operation of the fuel processor. The design strategy of prototype I will be used to develop a 1 kW class and 5 kW class fuel processor that is applicable to one family household or a small scale business building, respectively. Recently, prototype II has been manufactured and tested. Prototype II is designed to produce $1.0 \, Nm^3 \, h^{-1}$ hydrogen for a 1 kW class residential PEMFC under the operation condition of

Fig. 2. Appearance of the natural gas fuel processor for the 1 kW class residential PEMFC system, height: 500 mm, diameter: 250 mm.

flow rates were controlled by a high speed pump (RH0CKC head and driver, Fluid Metering Inc.). The temperatures of each unit were measured with thermocouples. The gas composition of the product gas at steady state was analyzed by an on-line

Table 1
Performance of the fuel processor at nominal load operation

Fuel processor type	Prototype I	Prototype II
Class	2.0 kW	1.0 kW
Volume of fuel processor (including thermal insulation)	o.d. 265 mm × H700 mm, 38 l	o.d. 250 mm × H500 mm, 25 l
Flow rate of NG for reforming (l min^{-1})	11.1	5.1
Flow rate of water for process (g min^{-1})	25.2	15.4
S/C ratio	2.5	3.0
Composition of product gas (vol. %, dry basis)		
H_2	71.4	72.9
CO_2	19.2	19.2
CH_4	4.3	2.3
CO	<10 ppm	<10 ppm
N_2	5.1	5.6
Methane conversion (%)	81	89
Fuel processing efficiency (%, HHV)	73	78
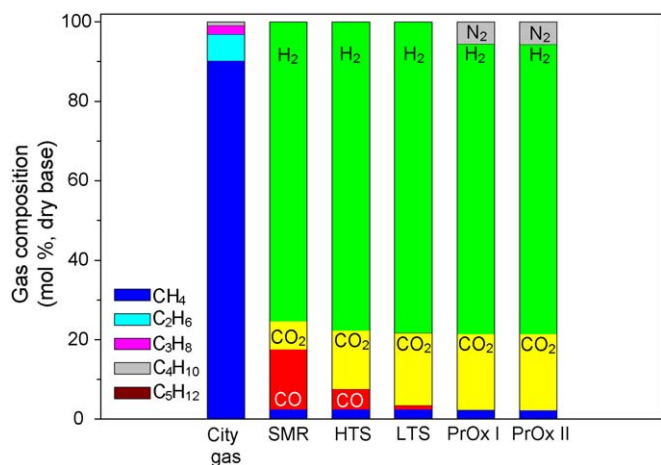
Fig. 3. The composition of product gas at the outlet of each unit during nominal load operation.
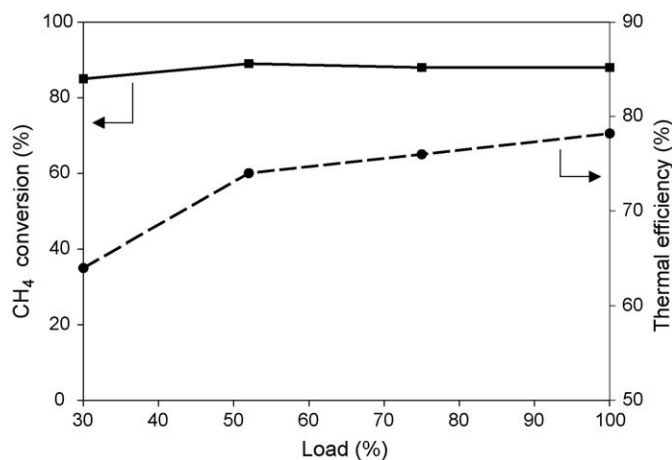

Fig. 4. Thermal efficiencies and methane conversions of the fuel processor under partial load conditions. ($\blacksquare$, solid line) CH_4 conversion; ($\bullet$, dashed line) thermal efficiency.

S/C = 2.5 and $[O_2]/[CO]$ = 1.5. The composition of the product gas from the fuel processor was described in Table 1, leading to a methane conversion of 89%. The outlet CO concentration of the steam reforming process is about 13.0 vol.%, which then reduced to ~1.0 vol.% with employing high and low temperature shift processes to produce more hydrogen.

Two-stage PrOx reactors adopting Pt- and Ru-based catalysts at each stage reduce the CO concentration below 10 ppm with the addition of air. In the first stage, a Pt-based catalyst reduces the CO concentration to 200–300 ppm at 180 °C, then the Ru-based catalyst removes residual CO to below 10 ppm at 140 °C. The Ru-based catalyst is used in the second stage to avoid the self-catalytic CO_2 methanation reaction that causes an abrupt temperature rise and unexpected H_2 consumption [9]. The amount of air at each stage corresponds to $[O_2]/[CO]$ = 1.5 and the total flow rate of air added to both stages is 0.11 $Nm^3 h^{-1}$. The composition of the product gas at each stage of fuel processing is shown in Fig. 3.

Table 2 and Fig. 4 show the performance of prototype II under partial load. At 75, 50, and 30% load operation conditions, the flow rates of natural gas for the process were set to 3.8, 2.5, and 1.5 l min^{-1}, respectively. At 75% load operation, the thermal efficiency was 76% and kept to 74% at 50% load

operation, which shows no serious decrease. However, the efficiency decreased to 64% at the 30% load operation due to a less effective heat transfer between the flue gas and the steam reforming process. Methane conversion decreased slightly from 89% at nominal load to 85% at 30% load. As for the CO removal performance, CO in the product gas was less than 10 ppm at all partial load operation conditions. Thus it is confirmed that the CO concentration is stable at less than 10 ppm under various operating conditions with the two-stage PrOx reactors adopting Pt- and Ru-based catalysts.

The time for start-up from cold to nominal load is about an hour with nitrogen gas. At the beginning of the start-up, nitrogen was used at the same flow rate as the natural gas for steam reforming process and then water is supplied to the fuel processor when the temperature of the low temperature shift process reached 100 °C. The water is evaporated and a mixture of steam and nitrogen enhances heat transfer of the combustion flue gas to the steam reforming and shift processes. After introducing natural gas for steam reforming, the outlet temperature of the steam reforming process slightly decreased, then reached steady state due to the highly endothermic reaction of steam reforming while the temperature of the shift and PrOx process was still rising and reached steady state within about an hour. The start-up time was
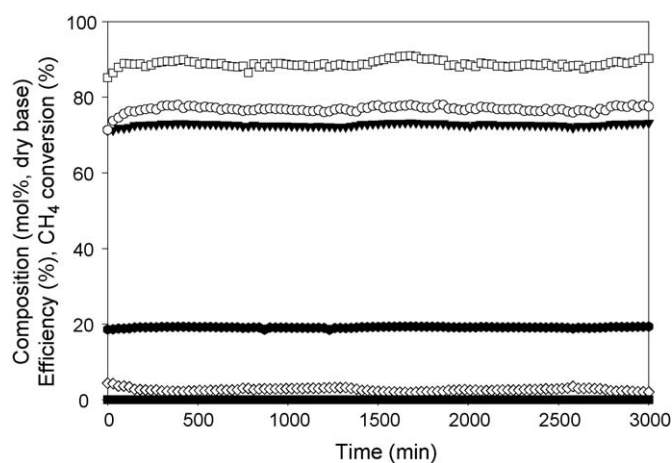
Table 2
Performance of the prototype II fuel processor under partial load conditions

Load (%)	75	50	30
Flow rate of NG for reforming (l min^{-1})	3.8	2.5	1.5
Flow rate of water for process (g min^{-1})	10.7	7.0	4.0
S/C ratio	3.0	3.0	3.0
Composition of product gas (vol. %, dry basis)			
H_2	73.5	73.2	72.8
CO_2	18.9	19.0	18.5
CH_4	2.5	2.1	3.0
CO	<10 ppm	<10 ppm	<10 ppm
N_2	5.1	5.0	5.2
Methane conversion (%)	88	89	85
Fuel processing efficiency (%, HHV)	76	74	64

Fig. 5. Durability of the fuel processor under nominal load conditions. Prototype II fuel processor with S/C = 3.0, [O$_2$]/[CO] = 1.5; (□) CH$_4$ conversion; (○) thermal efficiency, (▼) H$_2$ concentration, (●) CO$_2$ concentration, (◇) CH$_4$ concentration, (■) CO concentration.

about 2 h for prototype I and is shortened to 1 h by removing the unnecessary heat transfer area between the steam generator and shift processes and optimizing the heat exchange rate between the unit processes, which resulted in an increase of methane conversion and thermal efficiency.

The durability of the fuel processor was tested at nominal load. The composition of the product gas, thermal efficiency, and methane conversion were obtained after reaching the steady state. It is noted that the composition is stable for more than three days and the CO concentration in the product gas kept below 10 ppm during the operation. The stability of the fuel processor and the durability of the two-stage PrOx reactors have been confirmed with this operation (Fig. 5).

A long term durability of 10 years is the target for commercializing the residential PEMFC system. Therefore, the durability of the catalysts in each process is also important as well as the stability of the system. Moreover, continuous operation with load fluctuation is expected with a daily start up and shut down operation scheme for residential PEMFC systems. Accordingly, in future work, the durability of each catalyst, dynamic response of unit processes, and the reliability of the fuel processor against load fluctuation will be tested to confirm the stable performance of the fuel processor.

4. Conclusions

A fuel processor capable of delivering 1.0 and 2.0 Nm^3 h^{-1} hydrogen with a dual pipe geometry has been developed featuring an integrated structure of natural gas steam reforming, high and low temperature water gas shift reaction, steam generator and internal heat exchangers. The prototype I and II fuel processors gave a thermal efficiency and methane conversion of 73% as HHV basis and 81%; 78% as HHV basis and 89%, respectively. Two-stage cascade reactors employing Pt- and Ru-based catalysts, respectively, were used to remove CO to less than 10 ppm by preferential oxidation in both prototypes. At a partial load operation of prototype II, the thermal efficiency did not decrease below 74% until 50% load operation but decreased to 64% at 30% load operation, while the methane conversion kept to 85% even at the 30% load operation. The start-up time is about an hour for prototype II by improving the heat exchange rate between the unit processes. The durability of the fuel processing system is confirmed with a stable composition of product gas, especially the CO concentration which was kept below 10 ppm for 3 days.

References

[1] N. Shinke, S. Ibe, S. Takami, Y. Yasuda, H. Asatsu, M. Echigo, T. Tabata, Abstracts of 2002 Fuel Cell Seminar, Palm Springs, CA, 18–21 November 2002, p. 956.
[2] P. Devlin, 2005 Annual DOE hydrogen program review, Hydrogen production and delivery, 2005.
[3] T. Takahasi, Y. Nishzaka, K. Ito, N. Osaka, K. Kobayashi, H. Horinouchi, R. Toriumi, T. Miura, K. Nishizaki, Abstracts of 2004 Fuel Cell Seminar, San Antonio, Texas, 1–5 November 2004, p. 295.
[4] Y. Ikeda, T. Kiyota, A Kabasawa, Y. Chida, Abstracts of 2004 Fuel Cell Seminar, San Antonio, Texas, 1–5 November 2004, Poster session 1.
[5] G. Gigliucci, L. Pertruzzi, E. Cerelli, A. Garzisi, A. La Mendola, J. Power Sources 131 (2004) 62–68.
[6] A. Heinzel, B. Vogel, B. Hubner, J. Power Sources 105 (2002) 202–207.
[7] M. Echigo, N. Shinke, S. Takami, T. Tabata, J. Power Sources 132 (2004) 29–35.
[8] M. Echigo, N. Shinke, S. Takami, S. Higashichi, K. Hiral, T. Tabata, Catal. Today 84 (2003) 209–215.
[9] M. Echigo, T. Tabata, Appl. Catal. A: Gen. 251 (2003) 157–166.
[10] A. Heinzel, J. Roes, H. Brandt, J. Power Soures 145 (2005) 312–318.
[11] J. Mathiak, A. Hienzel, J. Roes, Th. Kalk, H. Kraus, H. Brandt, J. Power Sources 131 (2004) 112–119.
[12] Y.L. Yoon, J.H. Jeong, D.J. Seo, Y.T. Seo, Abstract of 9th Grove Fuel Cell Symposium, Westminster, London, 4–6 October 2005, p. 3.20.