Performance evaluation of integrated fuel processor for residential PEMFCs application

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ABSTRACT:

KIER has been developing the natural gas fuel processor to produce hydrogen rich gas for residential PEMFCs system. To realize a compact and high efficiency, the unit processes of steam reforming, water gas shift, and preferential oxidation are chemically and physically integrated in a package. Current fuel processor designed for 1kW class PEMFCs shows thermal efficiency of 78% as a HHV basis with methane conversion of 90% at rated load operation. CO concentration below 10ppm in the produced gas is achieved with preferential oxidation unit using Pt and Ru based catalyst under the condition of \([O_2]/[CO]=2.0\). The partial load operation have been carried out to test the performance of fuel processor from 40% to 80% load, showing stable methane conversion and CO concentration below 10ppm. The durability test for the daily start-stop and 8hr operation procedure is under investigation and shows no deterioration of its performance after 40 start-stop cycles.

KEYWORDS : Natural gas, Fuel processor, Steam reforming, PEMFCs, Residential cogeneration

Introduction

The fuel cell based power generation system is considered to be well qualified for a residential cogeneration system, which is generally incorporating the polymer electrolyte membrane fuel cells (PEMFCs) stack with hydrogen generation system from fossil fuels or renewable energy sources. PEMFCs based system has been widely developed because of its high efficiency, compactness, and reduction of air pollutants emission [1]. While introducing fuel cell systems into the market, small scale hydrogen generation system from various hydrocarbon feed stocks is required due to limited existing hydrogen infrastructures [2]. Many types of fuel processing system are being developed to meet quality of produced reformed gas that is pure enough for supplying to PEMFCs [3-5]. There exist well developed natural gas infrastructures in Korea, in which natural gas pipeline connected to the most of families and provide the hot water for heating by gas-fired boilers. Accordingly natural gas fuel processor adopting steam reforming process should be suitable for the residential PEMFCs system that requires high hydrogen concentration in reformed gas. Although the autothermal reforming process need relatively short start up time, the produced reformed gas contains less than 50% of hydrogen due to high content of nitrogen for internal combustion. Steam reforming process shows hydrogen concentration of about 75% in dry gas basis [6]. In case of steam reforming process, external burner is used to transfer the endothermic heat of reforming reaction and could avoid the failure of catalytic combustion and difficulties in maintenance. Accordingly the Korea Institute of Energy Research (KIER) is decided to develop a compact, integrated fuel processing system to provide hydrogen rich gas that can supply to PEMFCs system. The main focus of the work is to integrate the unit processes of a natural gas steam reforming, water gas shift, preferential oxidation, steam generator and internal heat exchangers into a single modular unit. In this project, the prototypes of fuel processor delivering 1.0Nm³/hr hydrogen were developed and tested to investigate the steady state behaviour at rated load operation. In parallel with the system integration, the steam reforming and CO preferential oxidation (PrOx) catalysts has been developed to improve the system performance. Especially the PrOx process is important to avoid the poisoning of PEMFC anode catalyst and guarantee the durability of PEMFCs cogeneration system. The Pt-based catalysts have been studied for CO removal process because of its high activity, in which CO was reduced to 100ppm with the addition of excess air corresponding to \([O_2]/[CO]=2\) and further reduced below 10ppm with additive air corresponding to \([O_2]/[CO]>3\), at which excess oxygen consumes hydrogen in reformed gas by oxidation and reduces the reforming efficiency [7]. Recently, it is reported that novel Ru catalyst has high CO removal performance in a single-stage PrOx reactor with additive air corresponding to \([O_2]/[CO]=1.5\) by
further reduction with gas mixture of hydrogen and nitrogen after aqueous reduction [8, 9]. However Ru catalyst also has undesired methanation activity for CO and CO₂, which is very sensitive with reaction temperature causing complex hardware for temperature control. In order to maintain low additive air amount and avoid complex control hardware, two stage PrOx reactors are adopted for the CO removal process. Pt-based catalyst is introduced to first stage with simple temperature control hardware and Ru-based catalyst is introduced to second stage without temperature control hardware. In this paper we report the characteristics of developed prototype fuel processors such as product gas composition and thermal efficiency. Also it is presented that the performance of lab-prepared Ru-based catalyst adopted at second PrOx reactor and the effect of support structure in PrOx reactions.

Experiments
1. Preparation of Ru-based PrOx catalyst
The Ru-based catalyst was prepared by impregnation method. RuCl₃ (RuCl₃·xH₂O, Aldrich Chem. co.) and 2~4 mm size of γ-Al₂O₃ granule were used as metal precursors and support. They were agitated for at least 0.5 hour and then the moisture was removed by rotary vacuum evaporator. The catalyst was further dried in oven at 110°C overnight and calcinated at 300°C for 4 hr. The same procedure was used to prepare the Ru-based catalyst with α-Al₂O₃ granule to verify the effect of the support structure. Catalytic activity was measured in a fixed bed flow reactor made of quartz tube under atmospheric pressure. 50 mg of the catalyst was placed at the center of reactor. The test gas is provided by mass flow controllers at a flow rate of 100 ml/min corresponding to GHSV of 120,000 hr⁻¹. The reactant gas mixture consists of 1 vol% CO, 1 vol% O₂ and 60 vol% H₂ in N₂ balance. To measure the preferential oxidation activity, the temperature of the reactor was increased to the desired temperature under test gas flow. The gas composition at the inlet and the outlet of the reactor at steady state was analyzed by a gas chromatograph equipped with TCD, methanizer and FID.

2. Fuel processor assembly
The basic engineering design concepts are to produce cascade heat flow and to maximize heat transfer efficiency between the heat sources (enthalpy of natural gas combustion, enthalpy of reformed gas, and exothermic heat from water gas shift reaction) and heat sinks (feeding water, natural gas and endothermic heat of steam reforming reaction) with minimization of heat loss to the ambient by integrating modularized unit processes. The schematic diagram of process flow of fuel processor is explained in Figure 1.

![Figure 1. Schematic diagram of fuel processor](image)

The Korean town gas was used as a natural gas fuel for testing the fuel processor and the composition of the city gas was generally 90.2 vol.% CH₄, 6.6 vol.% C₂H₆, 2.3 vol.% C₃H₈ and 0.9 vol.% C₄H₁₀ with 3.8 ppm of sulfur compounds as odorants. The THT and TBM are desulfurized in a bed of Mn-based adsorbent at room temperature. After preheating feed water to near boiling temperature using combustion flue gas and exothermic heat of water gas shift processes, the steam and desulfurized natural gas are mixed and introduced into the steam reforming process. The introduced hydrocarbons including CH₄, C₂H₆ and C₃H₈ are converted to H₂, CO, CO₂, residual CH₄ and H₂O on a Ru-based catalyst at about 700°C. The endothermic heat of steam reforming reaction is mainly supplied by the combustion heat of natural gas and air by an external burner. The reformed gases from steam reforming process pass through two consecutive processes of high and low temperature water gas shift reaction. The Fe-based catalyst reduce the CO concentration to 3~5 vol.% with high shift reaction rate and the CO concentration is reduced to below 1.0 vol.% by Pt-based catalyst, which is known to have high performance in shift reaction. By combining Fe and Pt-based catalyst, it is possible to reduce CO concentration below 1.0 vol.% without use of excess amount of
Pt-based catalyst. Air added to the outlet gas from shift processes and the mixed gas is provided to the PrOx reactors. The oxidation of residual CO by \( \text{O}_2 \) reduces the CO concentration in reformed gas to below 10ppm, which is needed to avoid the poisoning the anode catalyst of PEMFCs [7]. The two staged 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 easier temperature control of catalyst beds. The Pt-based catalyst is used for first stage and Ru-based catalyst is used for 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 integrated fuel processor with thermal insulation is shown in Figure 2. The two stage PrOx reactors are connected to the outlet of water gas shift reactors and the temperature control unit is deployed only in first PrOx reactor since the less exothermic reaction heat of second PrOx reactor can be easily removed without an aid of temperature control unit. A detailed description of fuel processor was given in previous paper [10].

![Figure 2. Appearance of the natural gas fuel processor for 1 kW class residential PEMFCs system](image)

The test of fuel processor with load fluctuations is carried out with automatic control of flow rates. Natural gas for external burner and steam reforming process was provided with mass flow controllers (Alicat Scientific), and air for external burner and PrOx processes was also provided with mass flow controllers (Alicat Scientific). The water flow rates were controlled by high speed pump (RH0CKC head and driver, Fluid Metering Inc.). The temperatures of each unit processes were measured with thermocouples. The gas composition of product gas at a steady state is analyzed by on-line gas chromatograph (HP 6890N system, Agilent Technologies Inc.) equipped with TCD, methanizer and FID using 8 vol% \( \text{H}_2/\text{He} \) as carrier gas. The detection limit of CO is 5 ppm. The CO concentration in reformed gas was also measured by infrared gas analyzer for insure the CO concentration.

**Results and discussion**

1. **Activity of the prepared Ru/Al\(_2\)O\(_3\)** catalysts

The CO preferential oxidation activity of \( \gamma \)-Al\(_2\)O\(_3\) supported Ru catalysts was tested at different Ru loadings of 0.5 and 1.0 wt% under the condition of \([\text{O}_2]/[\text{CO}] = 1.0\) and GHSV = 120,000 hr\(^{-1}\). As the reaction temperature was increased to 140°C, CO conversion of 1.0 wt% Ru catalyst reaches only 50% while maintaining 50% of \( \text{O}_2 \) consumption. However, when the reaction temperature rise to 160°C, CO conversion is greatly increased to 93% and reaches 99% at reaction temperature of 180°C with \( \text{O}_2 \) consumption of 100%. In case of 0.5 wt% Ru catalyst, CO conversion remains 85% even at reaction temperature of 180°C. It is noted that the added \( \text{O}_2 \) is completely consumed on both 0.5 and 1.0 wt% Ru catalyst at 160°C, but the CO conversion is much higher on 1.0 wt% Ru catalyst, which means CO was oxidized more effectively in 1.0 wt% loading and unnecessary hydrogen consumption is avoided. Therefore high CO removal conversion is achieved with 1.0 wt% Ru catalyst at a temperature range of 160°C and 180°C, which is the suitable condition for second stage of PrOx reactors because low exothermic reaction heat should be evolved after reducing CO concentration at first stage.

In addition with \( \gamma \)-Al\(_2\)O\(_3\) supported catalysts, \( \alpha \)-Al\(_2\)O\(_3\) was used to verify the effect of support structure on the activity of 2.0wt% Ru-based catalyst. The activities of CO preferential oxidation of \( \alpha \)-Al\(_2\)O\(_3\) supported Ru-
based catalyst under the condition of $[O_2]/[CO] = 1.0$ and GHSV = 120,000 hr$^{-1}$ are shown and compared with $\gamma$-Al$_2$O$_3$ supported catalyst in Figure 3. The Ru-based commercial catalyst showed good CO conversion of 100% at around 120°C, although the methanation of CO reduced the CO conversion above 140°C. Lab-prepared Ru-based catalyst on $\alpha$-Al$_2$O$_3$ showed 80% of CO conversion at 120°C and reached 98% at 140°C, while Ru-based catalyst on $\gamma$-Al$_2$O$_3$ showed 20% and 50% of CO conversion at each temperature. In contrast to Ru-based commercial catalyst, lab-prepared Ru-catalysts suppress the methanation reaction above 140°C and could maintain high CO conversion even at 180°C. Moreover the added O$_2$ is completely consumed on $\gamma$-Al$_2$O$_3$ supported catalyst above 120°C, which indicate that the CO molecules are converted to CO$_2$ more effectively on $\alpha$-Al$_2$O$_3$ supported catalyst under the investigated condition. The physical properties and microscopic characteristics of $\alpha$-Al$_2$O$_3$ supported Ru-based catalyst are under investigation. However this basic activity study showed the possibility of introducing the catalyst to PrOx reactors of fuel processor.

Figure 3. The CO preferential oxidation activities of Ru catalysts on various supports. (a) CO conversion, (b) O$_2$ consumption. Reaction conditions: 1.0 vol.% CO, 1.0 vol.% O$_2$, 57.0 vol.% H$_2$, N$_2$ balance, GHSV = 120,000 hr$^{-1}$ (dry base); (○) Ru-based commercial catalyst; (▲) 2.0 wt% Ru on $\alpha$-Al$_2$O$_3$; (■) 2.0 wt% Ru on $\gamma$-Al$_2$O$_3$.

2. Performance of fuel processors

Table 1 shows the performance of fuel processor at nominal load operations. It is designed to produce 1.0Nm$^3$/hr hydrogen under the operation condition of S/C=3.0 and $[O_2]/[CO]=2.0$. The composition of reformed gas at outlet of two staged PrOx reactors is 73.0 vol.% H$_2$, 19.5 vol.% CO$_2$, < 10 ppm CO, 5.5 vol.% N$_2$, 2.0 vol.% CH$_4$ leading the methane conversion of 91%. The thermal efficiency of fuel processor is defined as the heating value of the produced hydrogen referred to the heating value of produced hydrogen for reforming process and external burner, which is suitable to evaluate and characterize the stand-along fuel processing system without recirculation of the anode off gas [11, 12].

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

The outlet CO concentration of steam reforming process is about 13 vol.%, and then reduced to below 1.0 vol.% with employing high and low temperature shift processes at suitable operating temperature of 400°C and 250°C, respectively. Two stage PrOx reactors adopting Pt and Ru-based catalyst at each stage reduce the CO concentration below 10ppm with addition of air. In first stage, Pt-based catalyst reduces the CO concentration to 100~200ppm at 190°C, and then Ru-based catalyst removes residual CO below 10ppm at 120°C. The Ru-based catalyst is used at second stage to avoid the self-catalytic CO$_2$ methanation reaction that causes abrupt temperature rise and unexpected H$_2$ consumption [9]. The amount of air at each stage corresponds to $[O_2]/[CO]=2.0$ and total flow rate of air added to both stages is 0.10 Nm$^3$/hr.
Table 1. Performances of fuel processor at nominal load operation.

<table>
<thead>
<tr>
<th>Class</th>
<th>1.0 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of fuel processor (including thermal insulation)</td>
<td>O.D.250mm×H500mm (25 liter)</td>
</tr>
<tr>
<td>Flow rate of NG for reforming (liter/min)</td>
<td>4.3</td>
</tr>
<tr>
<td>Flow rate of water for process (g/min)</td>
<td>11.8</td>
</tr>
<tr>
<td>S/C ratio</td>
<td>3.0</td>
</tr>
<tr>
<td>Composition of product gas (vol. %, dry basis)</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>73.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.5</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.0</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>5.5</td>
</tr>
<tr>
<td>Methane conversion (%)</td>
<td>91</td>
</tr>
<tr>
<td>Fuel processing efficiency (% HHV)</td>
<td>78</td>
</tr>
</tbody>
</table>

Figure 4 shows the performance of fuel processor at partial load operations. At 80, 60, and 40% load operation conditions, the flow rates of natural gas for the process were set to 3.3, 2.5, and 1.8 l/min, respectively. At 80% load operation, thermal efficiency was 77% and kept to 74% at 60% load operation, which shows no serious decrease. However the efficiency decrease to 72% at 40% load operation due to a less effective heat transfer between the flue gas and steam reforming process. The methane conversion did not decreased seriously from 91% at nominal load operation to 90% at 40% load operation. As for CO removal performance, CO in the product gas was less than 10ppm at all partial load operation conditions. Thus it is confirmed that the CO concentration is stable less than 10ppm under various operating conditions with two stage PrOx reactors adopting Pt and Ru-based catalysts.

Figure 4. Thermal efficiencies and methane conversions of fuel processor at partial load operation. (■, solid line) CH₄ conversion; (●, dashed line) thermal efficiency

The time for start-up from cold status to nominal load is about an hour without nitrogen gas. At the beginning of the start-up, combustion flue gas was used to heat up the unit processes and then the water is supplied to fuel processor when the temperature of low temperature shift process reached 100°C. The evaporated steam enhances the heat exchange between unit processes of fuel processor. When low temperature shift process is ready for water gas shift reaction, natural gas is introduced to produce hydrogen rich reformed gas. After introducing natural gas for steam reforming process, the outlet temperature of steam reforming process slightly decreased, then reach steady state due to highly endothermic reaction of steam reforming while the temperature of shift and PrOx processed still rising and reach steady state. A stability of fuel processor was tested at nominal load operation for five successive days. The composition of product gas, thermal efficiency, and methane conversion were obtained after reaching the fuel processor steady state as shown in Figure 5. It is noted that product gas composition is stable and CO concentration in
the product gas kept below 10 ppm during the operation. The stability of fuel processor and two stage Prox reactors have been confirmed with this operation.

![Graph showing gas composition, conversion, and efficiency over time.]

Figure 5. Stability of fuel processor at nominal load operation under the condition of S/C=3.0, [O2]/[CO]=2.0; (○) methane conversion; (□) thermal efficiency; (▼) H2 concentration; (■) CO2 concentration; (▲) CH4 concentration; (●) CO concentration

Although the continuous operation with load fluctuations is expected during the day time, the power demand during the night time would be low and the efficiency of fuel processor should be not a best at this low load operation. Therefore daily start-stop operation is desirable for economic system operation that matches the power consumption patterns of household. The system would start up early in the morning before the power demand increases and stop during the night time. In this operation, fuel processor purge method is important for fast start up and safe shut down to remove inflammable gases in the fuel processor. Generally inert nitrogen gas is used for purge method, however it needs to avoid the high pressure nitrogen cylinder needing frequent exchange. As an alternative method, combustion flue gas is used during the start and stop operation and oxygen in the flue gas is removed to avoid the deterioration of fuel processor catalysts. Figure 6 shows the change in the product gas composition, methane conversion, and thermal efficiency of fuel processor for start-stop cycles. The fuel processor starts early in the morning and operated for about eight hours, then stop during the night time. The fuel processor is operated at rated load for three hours and then partial load operation is tested during the day time. After 40 start-stop cycles, the product gas composition is stable and the outlet CO concentration is below 10ppm. It is verified that the fuel processor can be operated without performance deterioration after 40 start-stop cycles and further studies are under investigation to test the durability of fuel processor for more than 1000 start-stop cycles without nitrogen purge.

Conclusions
Fuel processor capable of delivering 1.0Nm³/hr hydrogen with dual pipe geometry has been developed featuring integrated structure of natural gas steam reforming, high and low temperature water gas shift, steam generator and internal heat exchangers. The fuel processor shows the thermal efficiency and methane conversion of 78% as HHV basis and 91%, respectively. Two staged cascade reactors employing Pt and Ru-based catalysts, respectively, are used to remove CO less than 10 ppm by the preferential oxidation. At partial load operation, thermal efficiency did not decrease below 74% until 60% load operation but decreased to 72% at 40% load operation, while the methane conversion kept to 90% even at 40% load operation. The stability of the fuel processor is confirmed with stable composition of product gas, especially the CO concentration keeping below 10 ppm for five days operation. The durability of fuel processor for daily start-stop cycles is under investigation and at this time it shows no performance deterioration after 40 start-stop cycles. In parallel with the system development, the preferential oxidation catalyst is also developed and recent results indicate that 2wt% Ru-based catalyst supported on α-Al2O3 shows high activity in low temperature range and high CO selectivity. The effect of another support structures are under investigation to improve the current performance of catalyst and will be tested in fuel processor.
**Figure 6.** Durability of fuel processor for start-stop cycles at nominal load operation; (○) methane conversion; (□) thermal efficiency; (▼) H₂ concentration; (■) CO₂ concentration; (♦) CH₄ concentration; (●) CO concentration

**References**