

Purifier-integrated methanol reformer for fuel cell vehicles

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Abstract

We developed a compact, 3-kW, purifier-integrated modular reformer which becomes the building block of full-scale 30-kW or 50-kW methanol fuel processors for fuel cell vehicles. Our proprietary technologies regarding hydrogen purification by composite metal membrane and catalytic combustion by washcoated wire-mesh catalyst were combined with the conventional methanol steam-reforming technology, resulting in higher conversion, excellent quality of product hydrogen, and better thermal efficiency than any other systems using preferential oxidation. In this system, steam reforming, hydrogen purification, and catalytic combustion all take place in a single reactor so that the whole system is compact and easy to operate. Hydrogen from the module is ultrahigh pure (99.9999% or better), hence there is no power degradation of PEMFC stack due to contamination by CO. Also, since only pure hydrogen is supplied to the anode of the PEMFC stack, 100% hydrogen utilization is possible in the stack. The module produces 2.3 Nm³/h of hydrogen, which is equivalent to 3 kW when PEMFC has 43% efficiency. Thermal efficiency (HHV of product H₂/HHV of MeOH in) of the module is 89% and the power density of the module is 0.77 kW/l. This work was conducted in cooperation with Hyundai Motor Company in the form of a Korean national project. Currently the module is under test with an actual fuel cell stack in order to verify its performance. Sooner or later a full-scale 30-kW system will be constructed by connecting these modules in series and parallel and will serve as the fuel processor for the Korean first fuel cell hybrid vehicle. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Gasoline and methanol are considered as the two most promising energy carriers for fuel cell vehicles. Both liquids have to be reformed to hydrogen onboard the vehicle in order to be used as fuel for the fuel cell stack. While the former is considered to be the more practical option in the sense that the fuel infrastructure is already well established, the latter has the advantage that reformation of it is relatively easy. Currently many companies and research organizations worldwide are trying to develop the fuel processor converting those liquid fuels to hydrogen onboard the vehicle.

Fuel processor has three different branches as shown in Fig. 1. For gasoline, partial oxidation (Case 1) is known to be the only choice. Arthur D. Little has developed a multifuel processor [1] comprising three consecutive stages;

i.e., partial oxidation followed by a high- and low-temperature water–gas shift. They plan to combine it with a CO clean-up unit, such as preferential oxidation and test it for vehicle application. Although the actual performance is not well published yet, it is believed to have merits in fast start-up and response time.

On the other hand, for methanol, mostly steam reforming is applied (Case 2). This is because the reforming temperature is low (~ 250°C) and in practice the reformer is the shift reactor itself. Therefore, it is not necessary to put additional partial oxidation in front of it. Toyota [2] and Daimler–Benz [3] have successfully demonstrated onboard steam reforming of methanol combined with preferential oxidation in their prototype vehicles. It has merits in higher concentration of hydrogen and higher system efficiency. Argonne National Laboratory described its methanol processor as functioning by partial oxidation [4], but as mentioned above, the fact that it needs shift reaction before CO clean-up unit makes it not very practical. There is also autothermal reforming technology by Johnson Matthey [5], which combines the merits of steam reforming and partial oxidation.

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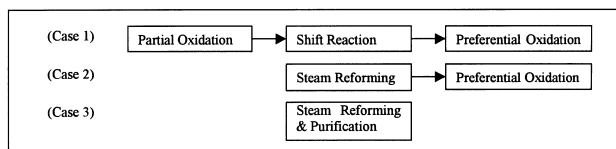


Fig. 1. Types of onboard fuel processors.

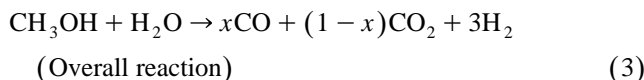
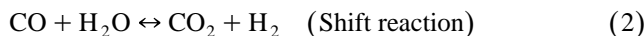
This study is about methanol fuel processor. Unlike other systems which have separate fuel reformer and CO clean-up unit, reforming and purification is done in a single reactor (Case 3) aiming to reduce the size of the system and to increase the overall thermal efficiency of the system. Twenty-five micrometers of palladium–copper alloy membrane has been fabricated into a module and incorporated in the reactor. Only hydrogen can permeate through the membrane so that hydrogen product from the reformer is essentially the same as the high-purity electronic-grade hydrogen. Due to the absence of any impurities, including CO, PEMFC stack can produce 30–60% more power than the case when CO content is 20 ppm [6].

Bleed gas from the reactor contains unrecovered hydrogen and rejected impurities. These are utilized as fuel for the combustion catalyst and supply heat for the steam reforming reaction. By adjusting the system pressure, hydrogen recovery by the metal membrane can be maintained at an optimum level, in which bleed gas is produced just enough to balance the heat requirement by the reformer. We achieved higher thermal efficiency than any other reported results, preventing any harmful pollutant from being exhausted from the system. SK Corporation already has multiyear experiences in fuel cell reforming technology [7] and in this study we achieved even more advances, making us ready to develop full-scale fuel processors suitable for fuel cell vehicles.

2. Underlying technologies

2.1. Steam reforming of methanol

In our system, methanol mixed with deionized water is evaporated by thermal exchange with exhaust gas. It is delivered into the reformer and the following reactions take place:



That is, methanol reforming is completed by (1) methanol decomposition (endothermic) and (2) water–gas shift reaction (exothermic). In order to achieve high conversion and high selectivity toward hydrogen, it is important to select conditions in which methane is not created and the product

gas does not recombine to methanol again. Also, operating conditions in water–gas shift reaction are highly important to maintain the desired yield of hydrogen [8]. Typically at pressures below 3 bar and temperature at 200–250°C, the molar ratio of $\text{H}_2:\text{CO}_2:\text{CO}$ is approximately 74:24:2.

To facilitate the above reactions, various kinds of reforming catalysts are used, but in this study $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst is used. This catalyst is inferior to $\text{CuO}/\text{ZnO}/\text{TiO}_2$ or $\text{CuO}/\text{Cr}_2\text{O}_3/\text{TiO}_2$ in terms of conversion and durability [9] but is easy to obtain since it is already commercialized and mass-produced. We plan to improve the performance of the catalyst by using better catalysts available in the market, or if necessary, developing a reforming catalyst for our own purpose.

2.2. Hydrogen purification by metal membrane

In general, CO content in the product hydrogen has to be below 20 ppm in order to be used as the anode gas for the PEMFC. Here, we applied a palladium-based alloy membrane to recover hydrogen selectively in the hydrogen-rich stream from the reforming reaction. There are several composite metal membranes which have hydrogen permeability sufficient for this purpose; for example, palladium-based alloy such as Pd–Cu or Pd–Ag, vanadium-based alloy such as V–Ni–Cr with palladium coated on the surface [10,11].

In this study, Pd–40Cu alloy membrane is used since it has been known to be the most reliable due to its high resistance against atomic expansion after repeated hydrogen absorption and desorption. The alloy ingot is first rolled to 25 μm of pinhole-free thin foil and, after several pretreatment steps, it becomes the metal membrane suitable for hydrogen separation. The membrane is then fabricated with copper frames to make a set of unit cells and assembled into the reforming reactor.

Hydrogen flux through Pd–40Cu membrane has been reported elsewhere [12]. In general the flux increases as the pressure gradient across the membrane increases or membrane temperature increases [13]. Fig. 2 shows hydrogen flux through the membrane as a function of hydrogen

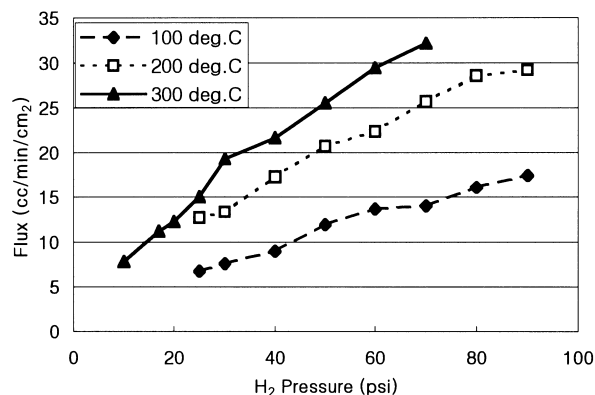


Fig. 2. Hydrogen flux through 25 μm Pd–Cu membrane.

partial pressure and membrane temperature. This result is for the case of pure hydrogen, but for the case of reformat gas, CO partly occupies the adsorption sites of the membrane surface so that the actual flux was found to be reduced by about 25%.

2.3. Catalytic combustion

Hydrogen containing bleed gas, which is not recovered by the metal membrane, is introduced to the catalytic combustion zone around the reactor. The combustion catalyst is highly active and completely oxidizes any combustible gases leaving only CO_2 and H_2O . Heat generated by the catalytic combustion is used to supply energy for the methanol steam-reforming reaction as well as to maintain the temperature of the metal membrane module.

When the whole system is cold, however, liquid methanol is sprayed through a nozzle and ignited by a glow plug to preheat the catalyst until it reaches minimum required temperature ($\sim 45^\circ\text{C}$) for combustion reaction. It takes only a few seconds and the flame is extinguished by powering off the glow plug. Subsequently, combustion continues by itself on the surface of catalyst. Methanol continues to be supplied as fuel for the catalytic combustion until a reformat stream is generated in the reformer. Afterwards, methanol is used only as the feed for the reforming reaction and bleed gas from the reactor acts as the heat source for the reaction. Therefore, combustion catalyst in this system has to be suitable both for methanol and reformer off-gas. We make the combustion catalyst by ourselves, in which a Pt-colloid solution is prepared first and then wash-coated on aluminum-containing steel mesh. Details of the preparation will be reported later.

3. System configuration and performance of the unit module

3.1. Design concept of the final product

The final goal of this study is to construct a 30-kW full-scale methanol fuel processor; it is planned to be completed by next year. Schematic diagram of the conceptual design for the full-scale system is shown at Fig. 3. The total system will consist of 10 unit modules and each module produces 3-kW-equivalent hydrogen. Air and bleed

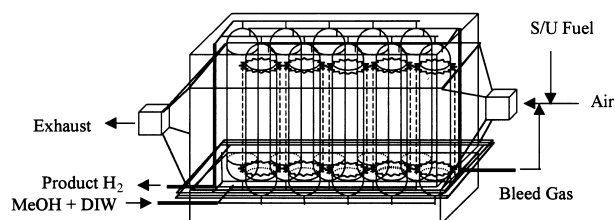


Fig. 3. Concept of 30-kW full-scale fuel processor.

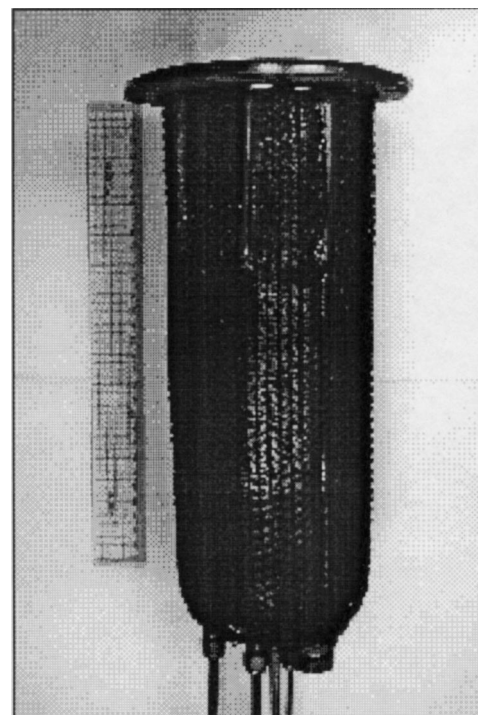


Fig. 4. Photograph of 3-kW purifier integrated methanol reformer unit module.

gas from the reactor is mixed at the entrance of the system. The mixture is evenly distributed over the combustion catalyst wrapped around each module and catalytically burned at a temperature around 500°C . Hydrogen produced from the system is $23 \text{ Nm}^3/\text{h}$ with purity the same as that of unit module (99.9999% or better). Exhaust from the catalytic combustion contains no pollutants such as CO, NO_x , nor any other combustible hydrocarbons.

Total volume and weight of this design are 40 l (0.75 kW/l) and 50 kg (0.6 kW/kg), respectively. Such power density is similar to those of previously demonstrated fuel processors by Toyota and Daimler–Benz but in the sense that it has higher thermal efficiency and produces ultra-high-purity hydrogen; much greater benefit is expected than other processors when it is combined with fuel cell

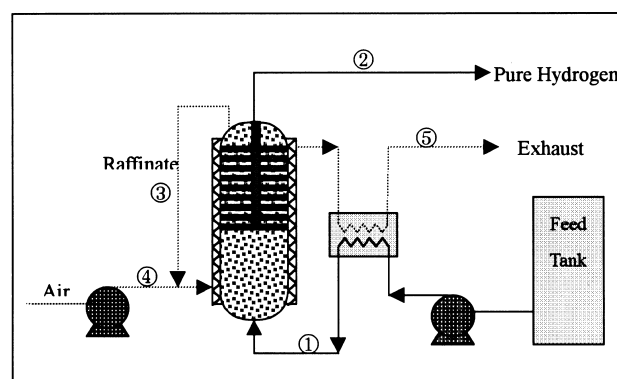


Fig. 5. Schematic diagram of unit module test station.

Table 1
Operating conditions at each stream (stream IDs are shown in Fig. 5)

Stream (ID)	Flow rate	Temperature (°C)	Pressure (atm)	Composition (vol.%)							
				MeOH	H ₂ O	H ₂	CO ₂	CO	O ₂	N ₂	
Feed (1)	45 cc/min	155	10	64	36						
Pure H ₂ (2)	33 NI/min	300	1			100					
Bleed (3)	33 NI/min	300	1	2	19	37	36	6			
Air (4)	125 NI/min	25	1						21	79	
Exhaust (5)	148 NI/min	80	1		7		13		12	68	

stack. In fact, with pure hydrogen, electricity generation efficiency of a given PEMFC can be higher than 43%. If the efficiency is 60%, then 23 Nm³/h of hydrogen production is equivalent to 43-kW capacity. Accordingly, the power density of the processor will also increase to 1.0 kW/l and 0.84 kW/kg. At the moment, performance of PEMFC is still improving, therefore, it is premature to estimate the equivalent capacity of our system. When integrated operation with the PEMFC stack is completed, more precise performance data about the system capacity will be determined.

3.2. Performance of unit module

A photograph of the 3-kW unit module is shown at Fig. 4. The total volume of the unit is 3.9 l and weighs 5.7 kg excluding flanges. Steam reforming catalyst and metal membrane units are installed inside the reactor and the wire-mesh-type combustion catalyst surrounds it. Flow channels inside the reactor have been designed to achieve optimal heat exchange with each other as well as the best hydrogen recovery.

To evaluate performance, the module was put in a separate vessel and a test station was constructed as shown in Fig. 5. Inside the reactor, thermocouples are installed at the lower, middle, and upper parts of the combustion catalyst, outer and inner parts of the reforming reaction section, and the temperatures are continuously monitored. The metal membrane is assumed to be isothermal with the hydrogen exiting from the reactor. Hydrogen content is measured in percent unit by TCD-type continuous monitor, Thermore 6N made by Maihak in Germany. Impurity contents (CO, CO₂, CH₄) are measured in parts per million by IR-type continuous measuring system, ZRH-1 Infrared Gas Analyzer made by Fuji Electric.

Table 1 describes temperature, pressure, and compositions of each stream. The unit module produced maximum 2.3 Nm³/h. Assuming the conversion efficiency of the PEMFC stack is 43%, it is equivalent to 3-kW capacity. The product hydrogen has been proved to be ultra pure with purity beyond 99.9999% and impurities level including CO was below its detection limit (1 ppm). According to mass balance calculated from the data shown in Table 1, methanol conversion in the reactor is approximately 95% and hydrogen recovery by the metal membrane is 75%.

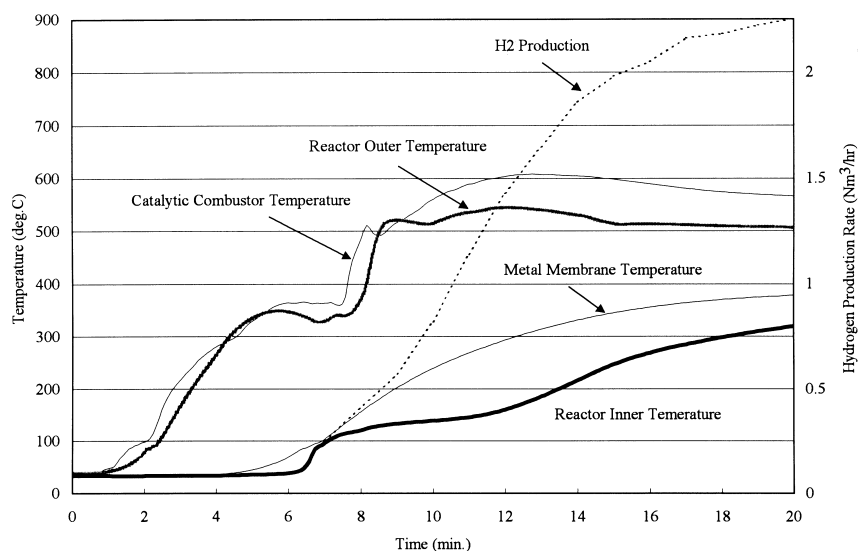


Fig. 6. Temperature excursion and hydrogen production rate from the cold start.

The unrecovered 25% of hydrogen is oxidized on the combustion catalyst. Therefore, the overall thermal efficiency of the system is 89% which is substantially higher than other published results.

Fig. 6 shows temperature excursion at each part of the reactor as well as the change of the hydrogen production rate from the cold-start until its maximum capacity. It takes 1 min to preheat the combustion catalyst by the flame ignition of methanol. Once the combustion catalyst is ready, the flame is extinguished and for the following 4 min the sprayed methanol is combusted on the combustion catalyst to continue preheating the reactor. Feed is supplied for 5 min when the outer temperature of the reactor reaches 350°C and product hydrogen starts to generate it within a minute. After 5 min from the feed supply, hydrogen production reaches 1 Nm³/h and after 15 min it approaches its maximum capacity (2.3 Nm³/h). Separate experiments have been conducted to check the response time by changing the feed rate (load following) and the restart characteristics after a short break (warm start). These have differed from case to case, but found that most of the transient responses are complete within a couple of minutes.

4. Conclusions

From this work, we developed 3-kW-equivalent purifier-integrated modular methanol reformer for fuel cell vehicles. It produces pure hydrogen at a rate of 2.3 Nm³/h with CO impurity less than 1 ppm. By integrating steam

reformer, metal membrane purifier, and combustion catalyst all in one reactor, a compact and easy-to-operate module has been constructed. A set of the unit modules can be assembled to a full actual capacity fuel processor. High thermal efficiency and near 100% hydrogen utilization by the stack make this system highly attractive for onboard fuel processor.

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