

Metal membrane-type 25-kW methanol fuel processor for fuel-cell hybrid vehicle

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Abstract

A 25-kW on-board methanol fuel processor has been developed. It consists of a methanol steam reformer, which converts methanol to hydrogen-rich gas mixture, and two metal membrane modules, which clean-up the gas mixture to high-purity hydrogen. It produces hydrogen at rates up to 25 N m³/h and the purity of the product hydrogen is over 99.9995% with a CO content of less than 1 ppm. In this fuel processor, the operating condition of the reformer and the metal membrane modules is nearly the same, so that operation is simple and the overall system construction is compact by eliminating the extensive temperature control of the intermediate gas streams. The recovery of hydrogen in the metal membrane units is maintained at 70–75% by the control of the pressure in the system, and the remaining 25–30% hydrogen is recycled to a catalytic combustion zone to supply heat for the methanol steam-reforming reaction. The thermal efficiency of the fuel processor is about 75% and the inlet air pressure is as low as 4 psi. The fuel processor is currently being integrated with 25-kW polymer electrolyte membrane fuel-cell (PEMFC) stack developed by the Hyundai Motor Company. The stack exhibits the same performance as those with pure hydrogen, which proves that the maximum power output as well as the minimum stack degradation is possible with this fuel processor. This fuel-cell ‘engine’ is to be installed in a hybrid passenger vehicle for road testing.

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1. Introduction

The advantages of using 100% pure hydrogen in a running fuel-cell system are numerous. Nevertheless, due to lack of suitable method for on-board hydrogen storage, not to mention the absence of a hydrogen infrastructure, fuel-cell vehicles to be commercialized in the near-term are expected as those with on-board fuel processors, which convert conventional liquid fuels to hydrogen gas. Since most present on-board fuel processors [1–4] cannot produce 100% pure hydrogen, they inevitably include impurities, either inert or toxic, in their product hydrogen. This is because they use preferential oxidation (PROX) for gas clean-up, which selectively converts CO to CO₂ in the product hydrogen. PROX is an effected way to remove the toxic impurity, CO, from the hydrogen gas, but it cannot avoid the incomplete eliminate CO, the inclusion of 30–50% of inert impurities, and the complexity of the system.

Impurities introduced in the product hydrogen significantly affect the performance of fuel-cell stacks. Most of PEMFC stacks show 20–50% capacity loss due to such impurities [5]. To reduce this loss in performance, the inclusion of a secondary ruthenium catalyst to the platinum catalyst at the anode and the addition of a small portion of air in the hydrogen has been tried [6]. Also, since the performance loss by the inert impurities is caused by an uneven distribution of hydrogen partial pressure across the stack, quite substantial efforts have been made [7–9] to develop optimal flow channels which minimize the pressure loss but still enable an even distribution of hydrogen. Despite these efforts, a consistent problems, such as a sharp surge of CO concentration on rapid load change which results in permanent damage of the stack, and low utilization of hydrogen due to bleeding-off the anode gas to avoid impurity accumulation in the stack still deteriorate the actual applicability of such processors.

The metal membrane-type fuel processor developed in the authors’ laboratories produces high-purity hydrogen, i.e. over 99.9995% purity. Moreover, the CO content is maintained below 1 ppm regardless of the operating conditions.

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Supply of such clean hydrogen to a fuel-cell stack enables maximum electric generation efficiency as well as enhanced lifetime of the stack. The use of high-purity hydrogen also opens the possibility that the fuel-cell stack can run dead-end, which means it can run without bleeding-off the anode gas. This is possible due to the absence of impurity accumulation in the stack. Such a feature can alleviate various complicated requirements in stack design. First, the decreased amount of total gas flow reduces the pressure drop across the stack and, accordingly, helps to reduce the size of the anode side gas channel in the bipolar plates. Second, the absence of other impurities ensures even distribution of hydrogen partial pressure across the stack, and hence gives more freedom in the channel design for anode gas flow.

The authors' research group has been working on on-board fuel processors for fuel-cell vehicles for several years. The major focus of the development is to apply proprietary hydrogen purification technology [10], and hence, to construct a premium fuel processor, which supplies ultra high-purity hydrogen to either PEMFC or alkaline fuel-cell (AFC) stacks. Based on previous studies of 2- [11] and 10-kW [12] prototype systems and various aspects of the actual operation conditions of fuel-cell hybrid vehicles, a 25-kW pre-commercial on-board fuel processor has been constructed. Here, we report the major design concept of the

unit and the result of performance tests. The critical difference of the 25-kW fuel processor to previous prototype units is that it has been designed to accommodate various restrictions given by the vehicle, such as limitations of utilities, space limitation, and the integration of control logic with other components. For example, since air is supplied to the processor by a blower with an inlet pressure that does not exceed 4 psi, the pressure drop along the air pass of the processor has to be maintained below 4 psi. The supply of the cooling water is limited so that the internal heat-exchanging has to be maximized. A photograph of the system is shown in Fig. 1. The whole system is installed underneath the car, and thus, the individual components are designed to be fit in their given spaces. The fuel processor has been integrated with 25-kW PEMFC stack and the operation characteristics are being investigated under various conditions that simulate actual operation in a car. The detail experimental results of such integrated operation will be reported later.

2. System configuration

In general, fuel processors for fuel-cell applications are composed of two major parts: a cracking unit and a purification unit. There are three different kinds of cracking unit, as distinguished by the type of oxidant: steam-reforming

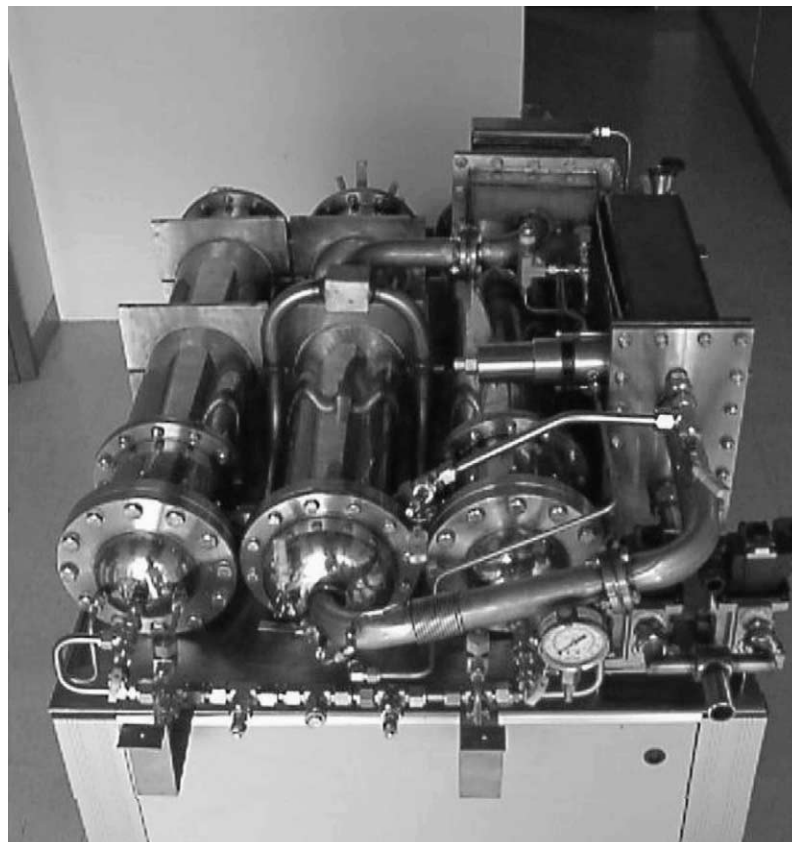


Fig. 1. Photograph of 25-kW methanol fuel processor.

(SR), partial oxidation (POX), and autothermal reforming (ATR). SR is an endothermic reaction in which water is used as the oxidant, whereas POX is an exothermic reaction in which air is used as the oxidant. ATR is a combination of POX and SR, in which a mixture of water and air in a certain ratio is used as the oxidant. The ratio is determined from consideration of the optimal thermal efficiency of the overall system. SR is usually selected as the cracking unit for methanol-fuelled vehicles due to its low reaction temperature and high thermal efficiency. Problems regarding slow start-up and the relatively sluggish dynamic response of SR units can be ameliorated by using a hybrid configuration for fuel-cell vehicles. The short-term dynamics of the vehicles is covered by batteries whereas the fuel-cell recharges the batteries at fairly stable conditions. The fuel processor developed in this study also uses methanol steam-reforming for the cracking unit. The catalyst used is ICI 33-5 M and the loading is 7 kg.

The purification unit can also be divided into different types of system, such as pressure swing adsorption (PSA), polymer membrane, metal membrane, solvent extraction, and preferential oxidation (PROX). Among these PROX is the most frequently used technology for fuel-cell applications, especially for vehicular applications. This is because of its compactness and relatively cheap cost. For gasoline fuel cells, a combination of POX and PROX is the predominant type of fuel processor and recently POX has often replaced ATR as the cracking unit. For methanol fuel cells, a

combination of SR and PROX is generally used for on-board generation of hydrogen. Since PROX removes not all the impurities but only CO, a metal membrane is used as the purification unit in this study, rather than conventional PROX.

A schematic of the 25-kW methanol fuel processor is shown in Fig. 2. Feed to the processor is a mixture of 63 vol.% industry-grade methanol and the 36 vol.% de-ionized water. This ratio results in 30% excess water, which helps drive the shift reaction toward its completion. This feed mixture is first preheated by heat-exchanging with the exhaust gas, which lowers the temperature of the exhaust, and hence, increases the thermal efficiency of the system. After the heat exchanger, the feed is still in a liquid phase although its temperature approaches the saturation value. The feed is ultimately evaporated in following evaporator in which a portion of the off-gas from the membrane purifier is mixed with air and catalytically combusted by a catalyst wrapped around the feed tubes. The amount of combustion can be adjusted by controlling the flow rate of the off-gas to the combustion catalyst. Any combustible components in the purifier off-gas, such as un-recovered hydrogen, un-converted methanol and CO, serve as the fuel for the catalytic combustion.

The vaporized feed mixture then contacts with the reforming catalyst on which the methanol cracking and water gas shift reactions take place to convert the methanol to a mixture of H₂, CO, CO₂, CH₄, unconverted methanol, and residual water. The gas mixture then enters the metal membrane units

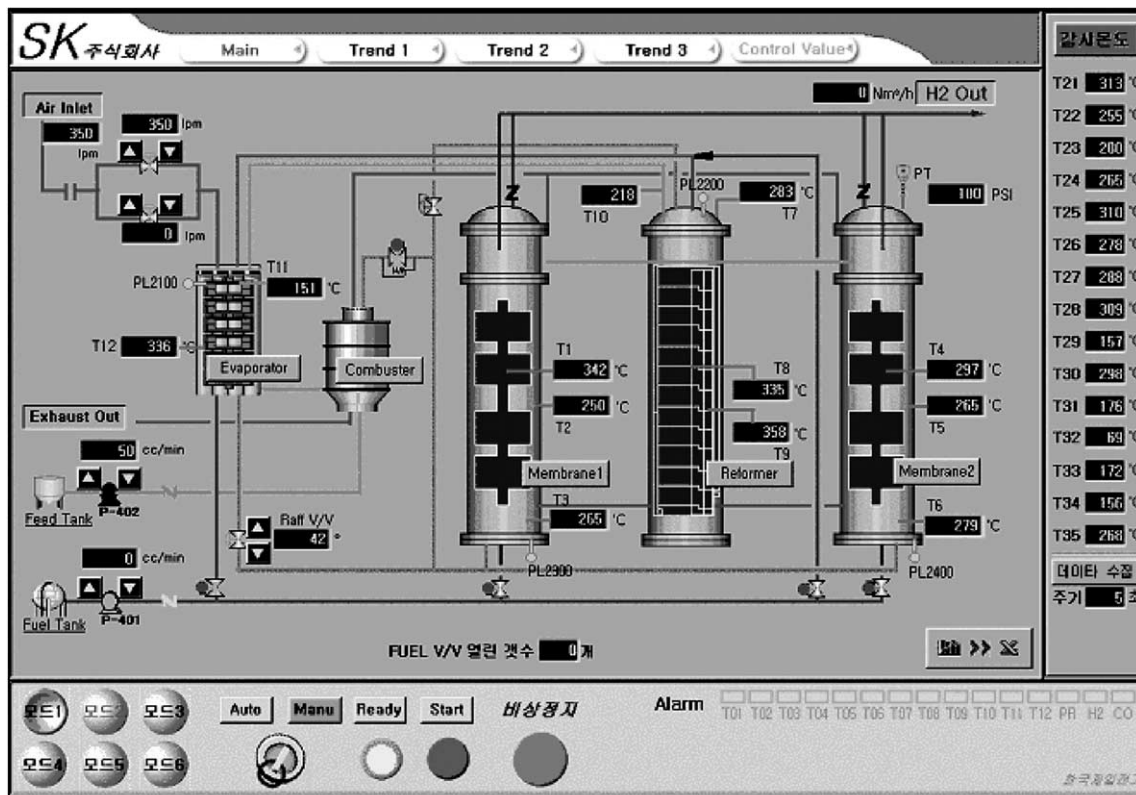


Fig. 2. Schematic diagram of 25-kW methanol fuel processor.

through which 70–75% of the inlet hydrogen passes and is collected as pure hydrogen. The temperature and pressure of the reformer and the metal membrane module are maintained at 300–350 °C and 130 psig, respectively.

The remaining 25–30% of the hydrogen and all other impurities in the inlet gas mixture compose the purifier off-gas. This returns to the combustion catalyst and any combustibles are burned in the combustion zones to evaporate the feed, to supplement heat for the reforming reaction, and to maintain the membrane module temperature. In case the amount of off-gas is insufficient, additional methanol fuel is injected to the evaporator to raise the temperature. In case of excess, the surplus is directed to an exhaust afterburner where any traces of combustibles are completely removed before the off-gas is mixed with the exhaust. Since the fuel content in the off-gas is dependent on the hydrogen recovery of the membrane purifier and the recovery can be simply controlled by adjusting the pressure of the membrane modules, once the system reaches a stable condition the use of additional methanol or afterburner treatment of surplus off-gas can be kept to a minimum. Most of the combustibles in the off-gas are completely combusted in the evaporator and in the reformer, and hence, the exhaust is basically clean and is composed of only CO₂ and H₂O.

For start-up, when there is no off-gas available, methanol fuel is used to heat up the reformer and the membrane unit. The methanol fuel is injected through a nozzle in the evaporator and ignited by the glow plug. Once ignited, the rate of fuel flow is increased quickly and the fuel is supplied to all of the combustion zones in the evaporator, reformer, and membrane unit. Since the fuel supply line is wrapped around the evaporator, once combustion starts the fuel is automatically evaporated in the line. Therefore, it is not necessary to pass the fuel through nozzles, instead it is directly mixed with the incoming air. The time required to raise the temperature to the normal operating condition is basically the start-up time of this fuel processor. In order to shorten the start-up time, the flow rate of the fuel should be as high as possible, but is limited by hot-spot development in the combustion zone at high fuel injection rates.

Combustion air is supplied so that the excess air is 30%. For initial start-up, however, more air is introduced in order to assure the complete oxidation of methanol fuel. Once the reactors reach their stable temperature and pressures, the methanol fuel is replaced by the purifier off-gas. Air-supply to the processor is 710 l/min at full-scale operation, and the pressure drop of the air across the system is designed to be below 4 psi. The air-supply line has an inner diameter of 1.5 in. and is connected in series in the sequence: evaporator, reformer, membrane units, afterburner.

3. Results and discussion

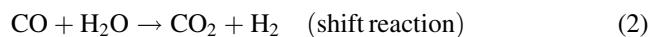
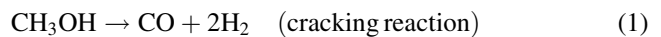
The typical conditions when the 25-kW metal membrane fuel processor is operated at its maximum capacity are given

Table 1
Typical condition of each stream in the fuel processor

	Feed	Reformate	Permeate	Raffinate
Flow rate	563 cm ³ /min	53 N m ³ /h	25 N m ³ /h	28 N m ³ /h
Composition				
CH ₃ OH	63%	1%	–	2%
H ₂ O	37%	12%	–	23%
H ₂	–	65%	99.9995%	31%
CO ₂	–	19%	<5 ppm	37%
CO	–	3%	<1 ppm	7%

in Table 1. The reformate is the hydrogen-rich gas mixture from the steam reformer, the permeate is the product hydrogen from the metal membrane purifier, and the raffinate is the off-gas from the purifier. The flow rate of the liquid feed mixture is measured by counting the weight loss of the feed mixture in the feed container as a function of time. The flow rates of gas streams are obtained by measuring the gas flows with a dry gas meter (Shinagawa's DC-2A) and then adding up the amount of condensable components. The condensable components are mostly unconverted methanol and excess water, and their amount can be calculated by sampling a certain portion of the gas stream, collecting the condensate during a certain time period, and analyzing the methanol concentration with a high precision refractometer (Belling Ham Stanley's RFM340, 25–40). The concentration of gaseous components in the reformate and the raffinate are measured by on-line gas analyzers (Fuji Electric's ZRH-1 IR gas analyzer for CO₂, CO, CH₄, and Maihak AG's Thermore 6N for H₂). For the detection of ppm-level concentrations of CO₂ and CO in the permeate stream, a high precision gas analyzer (Horiba's Trace gas monitor infrared analyzer GA-360E) is used.

In steam-reforming of methanol, two chemical reactions take place simultaneously as follows:



Adding reactions (1) and (2) we get



in which y is the shift conversion, and indicates the portion of CO which has been converted to CO₂ by the shift reaction (Eq. (2)). The ratio of CO₂ and CO given in Table 1 is equal to $y/(1 - y)$, and hence, the shift conversion (y) is 86%. Also, from the unconverted methanol in the reformate, it is found that the cracking conversion is 97%. Since the unconverted methanol and CO serve as fuel to supply heat for the endothermic steam-reforming reaction, the conversions are not necessarily correlated to the thermal efficiency of the system as long as the conversions are not too low to maintain the hydrogen partial pressure in the purifier.

The rate of hydrogen production as a function of the rate of feed supply is shown in Fig. 3. The production rate

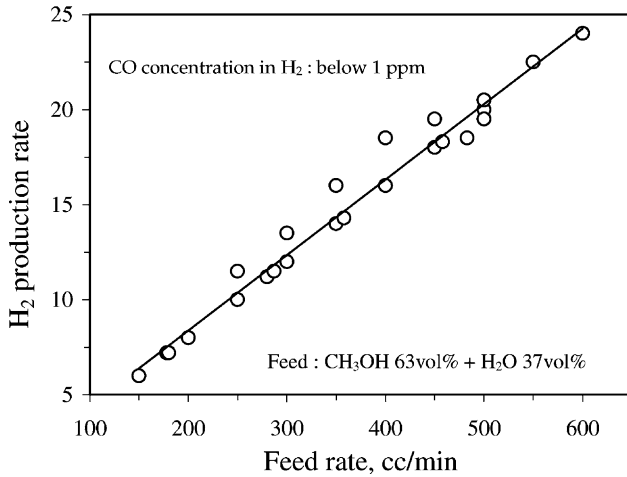


Fig. 3. Hydrogen production rate vs. feed supply rate.

displays a linear relationship with the incoming feed rate. This implies that, if this system is connected to a PEMFC stack, the final power output from the stack can be easily controlled by the feed supply rate. Also, it means that thermal efficiency of the processor remains constant regardless of the hydrogen production rate. From the slope in Fig. 3, the following correlation is obtained:

$$\begin{aligned} \text{methanol supply (cm}^3/\text{min)} \\ = 15.9 \times \text{H}_2 \text{ production (N m}^3/\text{h)} \end{aligned} \quad (4)$$

or

$$\text{methanol supply (mol)} = \frac{1}{3} \times 1.58 \times \text{H}_2 \text{ production (mol)} \quad (5)$$

Therefore, out of 1.58 mol of the methanol in the feed, 1 mol is used to generate product hydrogen and 0.58 mol is used either as the heat source for the reaction or lost as waste heat. The thermal efficiency of the fuel processor is defined as: HHV of hydrogen produced/HHV of methanol consumed or methanol consumed for hydrogen production and for heat supply/total methanol consumption. The high heating values (HHVs) of hydrogen and methanol are as follows:

$$\text{HHV(H}_2) = 68.3 \text{ kcal/mol} \quad (6)$$

$$\text{HHV(CH}_3\text{OH}_{(l)}) = 174 \text{ kcal/mol} \quad (7)$$

and hence, assuming 100% of thermal efficiency:

$$\begin{aligned} \text{methanol to be supplied (mol)} \\ = 0.393 \times \text{H}_2 \text{ production (mol)} \end{aligned} \quad (8)$$

or

$$\begin{aligned} \text{methanol to be supplied (mol)} \\ = \frac{1}{3} \times 1.18 \times \text{H}_2 \text{ production (mol)} \end{aligned} \quad (9)$$

From Eqs. (3), (7) and (9), it is noticed that out of 1.58 mol of methanol feed, 1 mol is used to make the product hydrogen, 0.18 mol is used to supply heat to the reactor, and 0.40 mol is

lost as waste. Therefore, the thermal efficiency of this fuel processor is $1.18/1.58 = 75\%$.

The maximum hydrogen production from the processor is $25 \text{ N m}^3/\text{h}$. The amount of energy in the product hydrogen is calculated by multiplying the heating value of hydrogen by its production rate, i.e.

$$25 \text{ N m}^3/\text{h of H}_2 = 762 \text{ kcal/h} = 89.0 \text{ kW}_{\text{th}} \quad (10)$$

This means that the thermal energy of $25 \text{ N m}^3/\text{h}$ of hydrogen is equivalent to $89 \text{ kW}_{\text{th}}$. If this is fed to a PEMFC stack, however, the actual electric energy output is dependent on the hydrogen utilization and the electric generation efficiency of the stack. In principle, the use of pure hydrogen may enable 100% hydrogen utilization and maximum electric generation efficiency. The maximum electric generation efficiency is in general over 45%, although it varies slightly with the intrinsic characteristics of the PEMFC stack. Therefore, it is possible to generate more than 40 kW of electricity when the processor is combined with an appropriate PEMFC stack. With the current state of stack technology, however, external humidification requirement of the stack hinders the dead-end operation and limits the hydrogen utilization to about 70%. This is because of partial drying of polymer membrane without an appropriate supply of moisture. Nevertheless, we believe that once the development of internal self-humidification is completed and the external moisture supply is no longer necessary, the electric generation from a fuel-cell stack combined with this fuel processor will be much higher than is currently available.

In order to test the stability of the system, the production of hydrogen was monitored continuously for a certain period of time at a fixed feed-supply rate. The results are shown in Fig. 4. The hydrogen production rate is quite stable over the time period although a slight increase is noticed. This demonstrates the reliable operation of the processor when combined with a fuel-cell stack. The slight increase is believed to be due to the slow warming up of the processor, which makes the system require less off-gas combustion to maintain the stable operating condition, and hence increased hydrogen recovery from the membrane purifier. After 1 h of

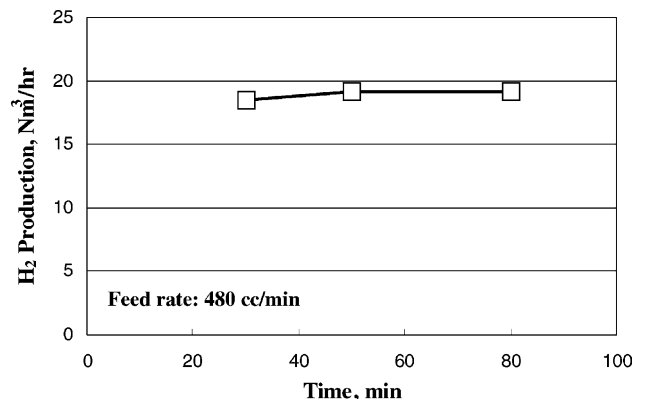


Fig. 4. Continuous operation of fuel processor at given feed rate.

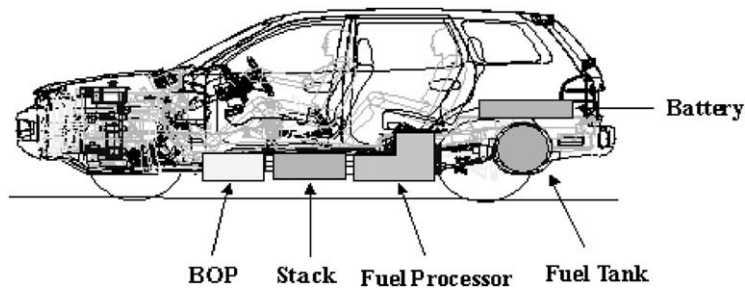


Fig. 5. Concept of fuel-cell hybrid vehicle.

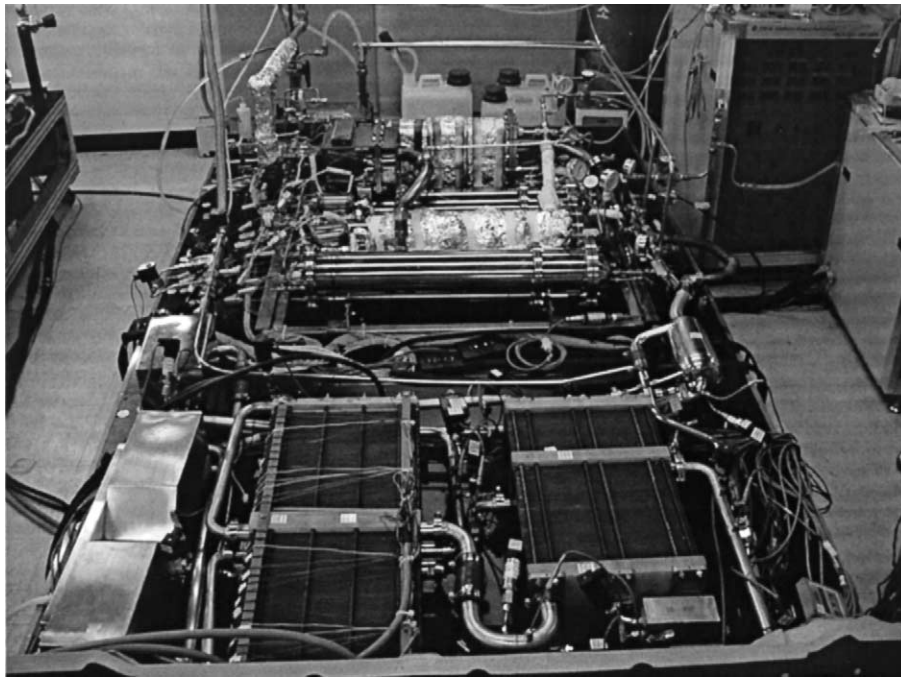


Fig. 6. Breadboard integration of fuel processor with PEMFC stack.

operation, the processor reaches a complete steady-state and there is no longer an increase in the production rate.

The 25-kW methanol fuel processor system is constructed relatively flat and this design is based on the consideration of the actual installation of the fuel processor at the bottom of a prototype fuel-cell hybrid vehicle. The prototype vehicle currently being considered is Hyundai Motor's sports utility vehicle named 'Santa Fe'. The engineering design for integrating the fuel processor in the vehicle is shown in Fig. 5. The fuel processor is located beneath the backseat of the vehicle. The secondary battery and the methanol tank are installed behind the processor and the PEMFC stack and a humidifier are located at the front. As a preliminary step towards vehicle construction, a breadboard combination of the fuel processor with a Hyundai Motor's PEMFC stack has been recently completed and tests of electricity generation from the combined system are currently in progress. A photograph of the combined fuel processor and PEMFC stack on a breadboard is shown in Fig. 6. Details of the

combined operation will be reported later. At present, the operation has been quite stable and the generation of 25-kW electricity from the combined system has been successful. Since the system has not been made fully automatic, it is not yet possible to evaluate the start-up time or the dynamic response of the system. Based on the experience of manual operation of the fuel processor, however, these functions are expected to be about 15 min for the cold start and about 2 min for 50% load change.

4. Conclusions

A methanol fuel processor for a 25-kW fuel-cell hybrid vehicle has been developed. The unit combines technologies for methanol steam-reforming, metal membrane purification, and catalytic combustion. Unlike other fuel processors, this metal membrane integrated fuel processor can produce high-purity hydrogen, which enables maximum power generation

and enhance lifetime from PEMFC stacks. In addition, the same operating conditions of the reformer and the purifier minimizes the dynamic control of the system which, in turn, makes the system more compact and reliable. Up to 25 N m³/h of over 99.9995% hydrogen with less than 1 ppm of CO contamination can be produced. The feed to the processor is a mixture of 63 vol.% methanol and 37 vol.% de-ionized water. The performance of the processor has been quite satisfactory in terms of the linear relationship between methanol feed rate and hydrogen production rate, stable operation over a period of time, and high thermal efficiency of the system. The thermal efficiency of the processor is approximately 75%, and when it is combined with a PEMFC stack, the overall power generation efficiency is expected to be over 45%. Integration with a PEMFC stack is in progress and the power generation from the combined system exhibits more than 25-kW power generation even with hydrogen utilization as low as 70%.

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