Zero-emission Fuel Cell Vehicle System Based on Nuclear Power System

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The possibility of a fuel cell vehicle system, which was capable to realize carbon dioxide zero-emission operation based on a nuclear power plant, was estimated experimentally. The system uses a portable thermally regenerative fuel reformer of carbon dioxide fixation type. The fuel cell system was expected to contribute on load leveling of nuclear power plant operation by utilizing surplus electricity of the plant as heat source for the thermal regeneration process. This study showed that the fuel cell system combined with nuclear power plants had potential to realize zero-emission energy system and to contribute to protection against global warming. The reactivity of calcium oxide with carbon dioxide was used in the regenerative reformer for the carbon dioxide fixation and also for heat source of fuel reforming. The reactivity of the reforming was examined experimentally to estimate the efficiency of the fuel reforming system based on a nuclear power plant.

KEYWORDS: zero emission, fuel reforming, calcium oxide, load leveling, carbon dioxide fixation

I. Introduction

Conventional energy supply system is changing drastically by recent development of fuel cell and micro-engine technologies and also enhancement of deregulation on energy supply. Decentralization of energy supply is popularized now1). Figure 1 shows comparison of energy supply scale between nuclear power plant and decentralized energy system2). The ordinate shows the electric output of each plant. Decentralized cogeneration plants (DCP) in the figure are operated in Denmark, which is the most developed country in the field of cogeneration. Conventional phosphoric acid fuel cell (PAFC), polymer electrolyte fuel cell (PEFC) and micro-gas turbine examples are shown as micro-scale energy system. Even an ultra small nuclear reactor in IAEA definition is large enough for decentralized energy system. Nuclear power system would be required to follow the decentralization. This study proposes a new fuel cell system based on a nuclear power plant. The system has a possibility to be a decentralized energy system with no carbon dioxide emission.

Fuel cells offer the possibility of expanding the electricity utilization market. Vehicles are seen as particularly good candidates for fuel cell application, because fuel cells are more compact, more quiet and emit cleaner exhaust gas than conventional internal combustion engines. One of the key technologies that will make the widespread use of fuel cells possible is a hydrogen supply system. The uses of liquefied or compressed hydrogen are candidates for this technology. However, the storage and transportation of either of these forms of hydrogen require large amounts of energy as well as stringent safety precautions. These drawbacks make steam reforming of common fuels, such as methane, propane, methanol and kerosene, more practical solution for storing and supplying hydrogen. Steam reforming can occur at the site of the fuel cell. The use of any of these chemical reactants as a hydrogen storage medium presents the possibility of a safe hydrogen supply system. On the other hand, the reforming requires additional apparatuses for hydrogen production, including at least three: a steam reforming reactor, a burner for reforming heat supply and a carbon monoxide converter.
In vehicles, it is especially important for a fuel cell reformer to be compact and lightweight. A concept of a thermally regenerative steam fuel reformer for a vehicle had been proposed\(^3\). A fuel cell system using the reformer can achieve zero carbon dioxide emission driving by chemical fixation of carbon dioxide and utilize of thermal output form a nuclear power plant.

This study estimated experimentally a possibility of the regenerative reformer system based on nuclear power plant. The PEFC is one of the candidate fuel cells for use in vehicles. This study is intended to apply the reforming concept on the PEFC. The contribution of nuclear power system on the fuel cell system was evaluated from experimental results.

II. Concept of Thermally Regenerative Reformer for a Vehicle

1. Regenerative Reformer

In this study, methane (CH\(_4\)) was chosen at first as a candidate reactant for steam reforming, because it is the most popular natural fuel resource and has a simple hydrocarbon fuel structure. The following regenerative reformer methodology is applicable also to kerosene and propane, both of which have reforming temperatures in the range of 700-900°C, similar to that of methane. The CH\(_4\) steam reforming process consists of the following two gas phase reactions with various catalysts.

Methane steam reforming:

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \leftrightarrow 3\text{H}_2(g) + \text{CO}(g),
\]

\[\Delta H^\circ = +205.6 \text{ kJ/mol} \quad (1)\]

Carbon monoxide (CO) shift reaction:

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{H}_2(g) + \text{CO}_2(g),
\]

\[\Delta H^\circ = -41.1 \text{ kJ/mol} \quad (2)\]

The study attempts to use calcium oxide (CaO) carbonation to remove carbon dioxide (CO\(_2\)) from the reformed gas and fix it.

Carbonation of calcium oxide:

\[
\text{CaO}(s) + \text{CO}_2(g) \leftrightarrow \text{CaCO}_3(s),
\]

\[\Delta H^\circ = -178.3 \text{ kJ/mol} \quad (3)\]

This study aims to cause Eqs. (1), (2) and (3) reactions in the same reactor at once. These reactions, taken as a whole, are defined as regenerative reforming.

Regenerative reforming:

\[
\text{CaO}(s) + \text{CH}_4(g) + 2\text{H}_2\text{O}(g) \leftrightarrow 4\text{H}_2(g) + \text{CaCO}_3(s),
\]

\[\Delta H^\circ = -13.3 \text{ kJ/mol} \quad (4)\]

Conventional steam reforming is depicted in Fig. 2 (a). CH\(_4\) and water (H\(_2\)O) react by Eq. (1) in a catalytic reformer, and the generated CO is shifted by Eq. (2) into CO\(_2\) and H\(_2\) in a catalytic converter. The endothermic reforming process needs a heat supply of \(\Delta H^\circ\). The proposed process is shown in Fig. 2 (b). This process consists of a reforming process (Fig. 2 (b-1)) while the vehicle is driving and a regenerating process (Fig. 2 (b-2)) for calcium oxide regeneration and carbon dioxide recovery while the vehicle is turned off. CaO and a reforming catalyst mixture are packed in a regenerative reformer. Reactants are reformed by Eq. (1), and generated CO\(_2\) is removed from the gas phase by the CaO carbonation of Eq. (3). The CO shift reaction of Eq. (2) is enhanced under the non-equilibrium condition realized by the CO\(_2\) removal. Purified H\(_2\) is generated from the reactor finally. The whole reaction of Eq. (4) is exothermic, hence the reaction needs no heat supply and can proceed spontaneously. A zero CO\(_2\) emission drive is possible due to CO\(_2\) fixation resulting from the carbonation. In the regenerating process, CaO is regenerated from CaCO\(_3\) in the reactor using high-temperature heat from surplus process heat or from surplus night electricity. Regenerated CO\(_2\) is managed according to a CO\(_2\) recovery process. The proposed regenerative reformer is intended to be contained in a removable package for use in a fuel cell vehicle.

The package is loaded into and recovered from a vehicle at a regeneration station that supplies new packages and regenerates used ones.

2. CO\(_2\) Zero-Emission Fuel Cell System

The concept of a CO\(_2\) zero-emission fuel cell system using the regenerative reforming process depicted in Fig. 2(b) is proposed in Fig. 3. The CO\(_2\) zero-emission system consists of fuel cell cars using packages of the regenerative reformer, a decentralized package regeneration station, and nuclear power systems for thermal energy supply. The regeneration station plays central role in the system. The packages are loaded in fuel cell vehicles. The vehicles are
Fig. 3 Carbon dioxide zero-emission fuel cell system using the thermally regenerative reformer driven by surplus electricity and heat from nuclear power plants.

Driven by hydrogen fuel produced from the packages. The packages after reforming are collected to the regeneration station. The packages are regenerated, that is, decarbonated thermally using electricity from commercial nuclear power plant and heat output from high-temperature gas reactor. Regenerated packages are reused repetitively in the cars. Generated CO2 is recovered in a storage vessel, and is treated at a hydrogenation process for methane regeneration or CO2 fixation processes. A comprehensive CO2 zero-emission system is formed using those CO2 treatment processes. A comprehensive CO2 zero-emission system is formed using those CO2 treatment processes.

The proposed reformer for vehicle fuel cells has several merits, as follows. The reforming process is simpler than conventional reforming systems. The power-generation efficiency of a fuel cell after with the reformer will be enhanced by the supply of the reformed high-purified hydrogen. In a conventional system, hydrogen effluent gas from the fuel cell is burned for the next reforming, because the CO2 concentration in the gas is too high for the cell to use. In the proposed system, the hydrogen concentration is high enough to supply high-purified hydrogen. The proposed system, on the other hand, the hydrogen concentration is higher than that of a conventional system, enabling the hydrogen to be consumed highly in the cell. Therefore, the proposed system also enhances the hydrogen economy of the fuel cell. As mentioned below, because the reformation equilibrium temperature is shifted to a lower temperature than in a conventional system, the exothermic CO shift reaction is enhanced naturally. Furthermore, the CO reduction induced by the enhancement is advantageous for fuel cell durability. Finally, because the fuel cell system using the proposed process emits no CO2 during operation, a CO2 zero-emission vehicle system could be established, so long as the treatment of CO2 is managed well after it is removed from the package. The proposed system in Fig. 3 would develop a new contribution of nuclear power plant on decentralized energy use.

The simultaneous reaction concept for hydrogen production from methane steam reforming had been patented by Williams. A fluidized bed concept using a reforming catalyst and carbon dioxide acceptor for hydrogen production was patented by Gorin, et al. Shift reaction and carbon dioxide removal in a single-reactor packed with a calcium oxide mixture were examined by Chun Han, et al. Calcium oxide as a CO2 absorbent was also applied to regenerative hydrogen production by Balasubramanian, et al. Those proposals were based on the use of the regenerative reforming process in fixed plants for hydrogen production, such as a fluidized bed or a combined system of a packed-bed reactor and gas turbine. Continuous batch-wise hydrogen production system using two regenerative reformers is proposed for a vehicle use by Specht et al. This study proposed a new concept of regenerative fuel cell use.

III. Experiment

A flow-type experimental apparatus for the steam reforming process shown in Fig. 4 was used for this study. A quartz tube, 15 mm in inner diameter and 1000 mm long, was used as a reactor. CaO particles and a reforming catalyst are packed in various forms in the reactor. Reaction gases controlled by mass-flow meters and water supplied by a
Three kinds of packed bed structures were discussed: (a) a conventional reformer type, (b) a sequential reformer type, and (c) a regenerative reformer type.

(a) Conventional reformer (CVR): The reactor was examined as a conventional reformer to allow for comparison with the proposed process. Alumina balls, 2.0 mm in diameter, were packed for pre-heating of the reaction gas. After the alumina ball layer was packed, 2.7 g of nickel catalyst, diluted with 21.9 g of alumina balls, was also packed. Ceramic wool pieces, 10 mm thick, were interposed between the ball layer and the diluted catalyst layer, and were placed also at both ends of the packed bed.

(b) Sequential reformer (SQR): The CO₂ removal performance of CaO carbonation after steam reforming was examined. At the downstream pass of the standard reformer structure, 8.1 g of CaCO₃ was charged.

(c) Regenerative reformer (RGR): The proposed process was examined in this reactor form. A mixture of 2.7 g Ni catalyst, 21.9 g alumina balls as a diluent and 8.1 g CaCO₃ was packed into the reactor after the alumina micro-feeder were mixed previously in an evaporator and supplied into the reactor. The reactor temperature was maintained by an electric furnace with an effective heating zone length of 600 mm. The temperature at the upstream end of the packed reactants, \( T \) [°C], was referred to as a representative bed temperature and was controlled by the furnace. The reacted effluent gas from the reactor was separated into liquid and gas. The separated gas flow rate was measured by a soap film flow meter, and the gas was analyzed by a TCD-type gas chromatograph (Shimazu GC-8A). Natural calcium carbonate (average diameter of 1.5 mm, purity over 98%, produced in Hiroshima, Japan, supplied by Nitto Funka Kogyo Co. Ltd.) was used in the reactor as the precursor to CaO. Nickel catalyst particles, screened to between 0.3 and 0.5 mm, were used for the reforming.

For the SQR and RGR type reformers, the decarbonation of CaCO₃ was proceeded prior to the reforming experiment, at 830 °C under argon flow of 100 ml/min for 4 h. The reduction of the catalyst was proceeded under H₂ flow of 100 ml/min for 60 min. after the decarbonation process. For all reforming processes, methane of 8.93×10⁻⁵ mol/min (20 ml (STP)/min), water of 3.57×10⁻⁶ mol/min (0.071 g/min) and argon of 8.93×10⁻⁵ mol/min (50 ml (STP)/min) were supplied to the reactor at bed temperatures of 550-750°C under atmospheric pressure.

The temperature in the bed was not uniform during reactions. The CaO carbonation, which showed the highest temperature change in Eqs. (1)-(4), had been discussed in a previous study. The bed temperature change under this study conditions was estimated less than 10°C at a peak period. The temperature at the upstream end of the packed bed was regarded as the representative bed temperature (\( T \)) in this study. The reforming performances of all three types of reformer were then assessed experimentally.

IV. Results and Discussion

1. Regenerative Reforming

Figure 5 shows an example of a temporal change in the concentrations in effluent of the regenerative reforming at 550°C. Time 0 min. indicates the start of reactants supply to the reactor. The dashed lines show hydrogen equilibrium concentrations in RGR and CVR, respectively.

During the initial 60 min., charged CaO absorbed well CO₂ by carbonation, then, the concentration of CO₂ and CO were less than 1% each, and the hydrogen production was higher than the equilibrium concentration of standard reforming. Because CO₂ adsorption kept the gas phase non-equilibrium, the shift reaction, steam reforming reaction and hydrogen production all proceeded beyond the original standard equilibrium composition.

As the carbonation was saturated after 70 min., the steam reforming and shift reactions changed into a standard
reforming condition, and the hydrogen production decreased below the standard equilibrium. The length of the non-equilibrium period depends on the amount of packed CaO. The amount in this study was chosen in order to maintain the non-equilibrium condition for more than 60 min. For the following discussions, we used the concentration around 30 min. of the reforming period as the representative reforming value.

2. Comparison of Reforming Performance

The reforming performances of the conventional, sequential and regenerative reformers were compared from analysis of the gas product of these reformers.

(1) Change in carbon dioxide concentration

Figure 6 shows dependency on the CO₂ concentration change in the effluent gas on reforming temperature. The solid and blank dots show measured and equilibrium values. The CO₂ concentrations in the SQR and RGR at 550 and 650°C are lower than that in CVR because of the CO₂ adsorption resulted from the CaO carbonation.

The CO₂ concentration of RGR at 550°C was less than 1%. In RGR, the exothermic heat of CaO carbonation was consumed well by the endothermic CH₄ reforming, and the bed temperature was kept relatively low, enhancing CO₂ carbonation. In SQR, on the other hand, the CaO bed temperature was higher than that of RGR because CaO carbonation raised the bed temperature relatively high, thus the CaO carbonation itself was inhibited more than was the case in the RGR. The CO₂ concentration in the RGR at 650°C was lower than that of equilibrium, because endothermic CH₄ reforming proceeded well and the bed temperature was lower than those of the others, and CO₂ absorption by CaO carbonation was enhanced.

The equilibrium lines, which show the reactions in Eq. (4), are bent at 725°C because above this temperature the equilibrium CO₂ pressure of Eq. (3) is higher than the partial pressure of CO₂ in the reforming equilibrium composition, and the CaO effect on the reforming disappears. Then, at 750°C, the concentrations were almost the same between CVR and SQR, which showed that CaO carbonation stopped above that temperature. The slightly higher CO₂ concentration seen in the SQR than in the CVR is attributed to a catalytic effect of CaO on the methane reforming.

(2) Change in hydrogen concentration

The changes in hydrogen production in effluent gas are shown in Fig. 7. The concentrations of H₂ with the CVR, SQR and RGR increased in this order. The H₂ production performance of the RGR was outstanding at low temperatures. Especially, 94% of H₂ was measured in the RGR at 550°C. CaO carbonation removed CO₂ from the gas phase, and enhanced CO shift reaction in Eq. (2) and also CH₄ reforming in Eq. (1). Simultaneously, the exothermic heat of carbonation and the heat of the shift reaction compensated well for the endothermic reforming. The heat being exchanged between the reactions enhanced both reactions each other. At 650°C, the exothermic CO shift reaction and CaO carbonation rates were smaller than they were at 550°C, and CH₄ reforming was inhibited due to the surplus CO in the reaction gas phase. Thus, the hydrogen production with the RGR was close to that with the SQR. The unique performance of the RGR was available at a lower temperature.

3. Performance Evaluation of the Regenerative Reformer

Performance evaluation for the regenerative reformer based on the experimental results of this study is shown in Table I. The RGR reactor volume required for a vehicle fuel cell, which needs 1.0 kg of H₂ in order to drive for 100 km, was evaluated from the experimental analysis. The estimation assumed that all of the produced H₂ was consumed in the fuel cell. From this estimation, 7.46 kg (9.04 liters) of CaO was required for the RGR. The CaO requirement calls for similar amounts of total reforming reactants both CH₄ and H₂O. The capacity of a conventional hydrogen bomb under 15.2 MPa requires 74.7 liters to store the same amount of H₂. Thus the RGR system is expected to provide a more compact and
lightweight container than the conventional H₂ storage system.

Estimated contribution of a nuclear power plant on the fuel cell system is shown in Table 2. The estimation assumed that nighttime surplus electricity from a nuclear power plant of 1 GW electric output was used for the regeneration of the reformer for 8 h. 1.3×10⁶ pieces of the reformer package are regenerative by the power plant. Over 7,000 ton of CO₂ is recoverable from the process. The fuel cell system with a nuclear power plant would have effective contribution on reduction of CO₂ emission and protection against the global warming. For practical estimation of the reformer performance, inert gas in the reactant and higher operation pressure should be taken into account. The removal of inert gas should enhance both CaO carbonation and CO₂ removal. On the other hand, hydrogen production might decrease at higher pressure. A more detailed examination will be necessary to determine which effect is dominant under practical conditions. The enhancement of durability of CaO reactant to the repetitive reversible reaction would be important subject also for practical use. Conventional CaO reactant loses reactivity easily under repetitive reaction cycle. The reactivity disappearance would be arisen from sintering between reactant primary particles by relatively high-temperature reaction. An economical enhancement of reaction durability to the sintering is required.

The RGR is applicable for higher-hydrocarbon fuels, such as propane and kerosene. Because CaO is capable of reacting with sulfur components, the RGR can contribute to the purification of hydrogen product by removing sulfur components contained in an original fuel. The RGR system offers the possibility of realizing a CO₂ zero emission vehicle system and enhancing the utilization of surplus energy. A battery-powered vehicle is a practical zero emission car. Compared with a battery-powered car, the RGR system could be more compact, and also regenerative by surplus thermal energy. High-temperature gas reactor is a candidate of heat sources for the regeneration. Direct use of thermal energy generated from the gas reactor enhances energy use efficiency compared with electricity use from nuclear power plants.

V. Conclusion
A fuel cell system using a regenerative fuel reformer based on a nuclear power plant was proposed. The performance of the regenerative reformer was demonstrated experimentally. The regenerative reformer was applicable at a lower temperature than common reformers was and produced high-concentration hydrogen of 94% with less than 1% each of CO and CO₂. The required amount of CaO for the reformer was expected to be similar to the total weight of methane and water as fuel resources. The reformer capacity would have small effect on load of the vehicle.

The system can utilize surplus electricity generated from commercial nuclear power plant. Electricity of 1 GW for 8 h can regenerate 1.3 million of reforming packages. The fuel cell system would widen need of nuclear power plant because the system realizes new vehicle system of total CO₂ zero-emission. The fuel cell system also contributes to load leveling of nuclear power plant operation, and improvement of the value of nuclear power system.

| Table 1 Estimated size of the regenerative reformer for FC vehicle |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Vehicle mileage [km] | 100 | Hydrogen requirement [kg] | 1.0 | CaO requirement mass [kg] | 7.94 |
| Requirement reaction heat [MJ/piece] | 22.3 | Number of cell piece [pieces] | 1.29×10⁶ | Recovered CO₂ amount [m³ (STP)] | 3.62×10⁶ |

| Table 2 Estimated contribution of a nuclear power plant on the FC system |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Power plant | 1.0 | Night time operation duration [h] | 8.0 | Requirement reaction heat [MJ/piece] | 22.3 | Number of cell piece [pieces] | 1.29×10⁶ |
| Recovered CO₂ amount [ton] | 7.12×10³ |

Nomenclature

| CVR | conventional reformer |
| c | mole concentration in effluent gas excluding inert gas [mol%] |
| DCP | decentralized cogeneration plant |
| PAFC | phosphoric acid fuel cell |
| PEFC | polymer electrolyte fuel cell |
| RGR | thermally regenerative reformer |
| SQR | sequential reformer |
| T | bed temperature measured at the upstream end of reactor bed [°C] |
| ΔH° | standard enthalpy change [kJ/mol] |

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References


