A Compact Reformer for Portable Fuel Cells

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Abstract

A compact reformer to generate hydrogen for portable fuel cell applications is presented. This reformer is a conventional type single-path tubular reactor packed with granular catalyst particles in which steam reforming and catalytic partial oxidation reactions take place in series using a mixture of methanol and water as a feed. The novel feature of this reformer is in the interlacing of the flow path for efficient heat transfer between the reactor sections where the endothermic steam reforming reaction and the exothermic partial oxidation reaction are taking place respectively. Experiment using a commercial catalyst (CuO/ZnO/Al2O3) showed a feed conversion as large as 85% at an operating temperature of 250˚C or below, and the hydrogen concentration higher than 75% in the product gas. Observed pressure drop for the gaseous flow through a packed tube agrees well with a theoretical prediction.

Introduction

Fuel cell emerged as an important technological area because of its capability to convert chemical energy directly into electrical energy with a higher efficiency than the conventional thermomechanical-electric devices.[1] There are many different types of fuel cells depending on the electrolytes used for each type of fuel cells. Among those, proton exchange membrane fuel cell (PEMFC) is of interest for the present study. PEMFC, which is also known as polymer electrolyte membrane fuel cell, offers much higher power density than other types of fuel cells. In addition, the intrinsic properties of the materials used for PEMFC make them to operate at a low temperature between 60~120°C. This low operating temperature allows quick start-up and rapid load-response which are main advantages of PEMFC. Because of its low temperature operability, PEMFC is favored as a portable power source for the applications as in aviation, automobile, and consumer electronics (e.g. laptop, cell phones, etc…). In fact, only PEMFCs may meet the requirements for such portable applications which are compact size and lightweight besides low temperature operability.[1-4]

The best fuel for PEMFC is pure hydrogen as for all other type of fuel cells. However, the storage of hydrogen as well as the portability of the hydrogen storage system are rather problematic for small-size mobile applications. Thus, hydrocarbons, especially methanol or methane, are recognized as more practical choices as a fuel for PEMFCs. Use of methanol or other hydrocarbon fuels, however, requires a reformer unit by which hydrogen is produced. It is an additional unit that not only increases the system size but also creates other technical difficulties such as CO-poisoning of catalyst. Recent advances in various areas including catalyst technology have resolved many of the difficulties although there still exist some obstacles that require research efforts at a fundamental level. Between methanol and methane, methanol may be more favorable because it is in liquid phase at standard condition.[5-8]

A commercially viable portable reformer requires high efficiency in terms of conversion of hydrocarbon fuel and thermal management, compactness, and easy integration with the fuel cell. Present study is to investigate a new design idea for a compact reformer using methanol and water mixture as the fuel. Flow simulation was conducted to determine various design features including the dimension of the reformer that can be used for a PEMFC with the energy production capacity of 10 Watt at 50% efficiency. Subsequently, a prototype reformer was built to confirm the simulation results and to assess the efficacies of new design features. Experiments were conducted with a commercial catalyst (CuO/ZnO/Al2O3) from Süd-chemie.

A Compact Reformer

The well-known reaction to produce hydrogen from methanol is the stream reforming reaction:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad (\Delta H_0 = 130.9 \text{ kJ/mol}) \tag{1}$$

The steam reforming reaction can be followed by a reverse shift reaction that is an undesirable side reaction:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{2}$$

CO generated by this reaction should be removed as it acts as a catalyst poison. The steam reforming reaction occurs at about 200~300°C and preferably at an elevated pressure of 3~4 bar. And it is an endothermic reaction requiring external heat supply. Although the heat can be supplied by an external source through the partial use of the electric power generated by the fuel cell., the catalytic partial oxidation (CPOX) of methanol that is highly exothermic (autothermal reforming) can be combined with the steam reforming reaction:

$$CH_3OH + \tfrac{1}{2} O_2 \leftrightarrow CO_2 + 2H_2 \quad (\Delta H_0 = -\, 154.9 \text{ kJ/mol}) \tag{3}$$

One of the difficulties in making a compact reformer is the difficulty in catalyst incorporation and low catalyst efficiency associated with small contact area when surface coating method is applied. One idea to increase the catalyst efficiency is the conventional tubular reactor in which granular catalyst particles are packed in cylindrical reaction channels. In order to make a reformer to be self-sustaining without an external energy source, the exothermic CPOX may be induced along with the endothermic steam reforming reaction. A new reformer proposed here may be capable of achieving these two requirements (i.e., improved catalyst efficiency and self-sustainability) is shown schematically in Figure 1. It consists of two types of basic plates; the reactor plate and the end plates (front and rear plate in Figure 1). The straight cylindrical channels in the reactor plate are filled with catalyst particles and the stream reforming and CPOX reactions take place in the channels. The front and the rear plates have many grooves that connect two neighboring cylindrical channels thereby changing the flow direction back and forth and forming a long meandering reaction path. The back and forth layout of channels make full utilization of space, which is necessary for the reformer to be compact enough for portable application of PEMFC.

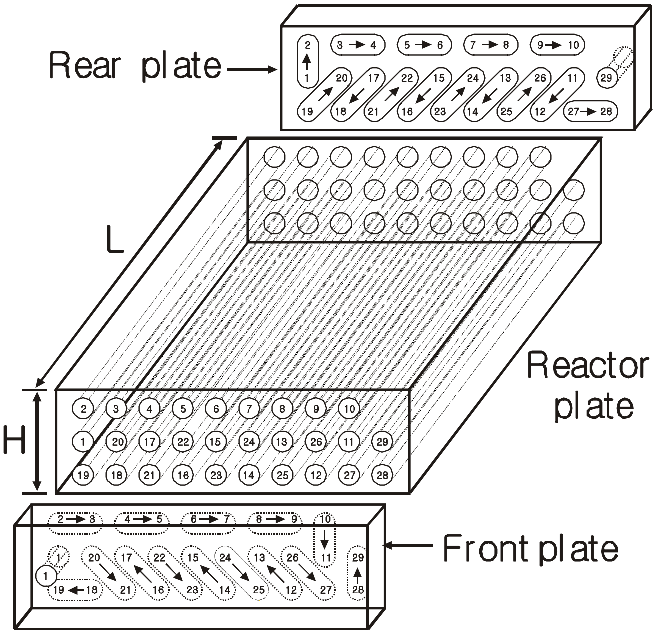

Figure 1 Schematic of the proposed reformer channel layout

The most important design feature of this reformer is the layout of the grooves that enable the interlacing of the flow channels. The numbers, 1 through 29, written on each cylindrical channel indicate the sequential order of the flow path through which the reactant will flow. Reactants are fed into channel #1 of the reactor through the hole (#1) in the front plate. Then they flow through the channels in the top row #2 to #10 where they are vaporized. (Although not shown in the figure, the reformer also uses a thin film heater attached on the top surface of the reactor plate. The heater is to supply heat for the evaporation of methanol/water mixture and heat up the reformer to an appropriate operation temperature for the initial start-up.) The vaporized reactants then flow into channel #11 and flow sequentially from #11 to #18. The slant grooves in the end plates make these flow channels #11 through #18 to be alternating in rows and skipping immediately neighboring channels in the same row. The reactants then flow into channel #19 and sequentially from #19 through #28. Channels #19 through #28 are again alternating in rows and skipping immediately neighboring channels in the same row due to the end plate groove layout. By then, the reactions are complete and the reaction products flow through channel #29 and exit the reactor through the hole (#29) in the rear plate. We may notice that channels #11 through #18 are interlaced with the channels #19 through #28.

The feed contains oxygen which is supplied from the air, and the partial oxidation reaction is dominant over the steam reforming reaction in the presence of oxygen. Thus, until the feed oxygen is depleted, the exothermic CPOX is the main reaction that occurs in the channels #11 through #18 where heat is generated. (We assume the CPOX reaction will be completed in the channels #11 through #18, however, it may need more or less channels for the reaction to be completed.) Once oxygen is depleted, only the endothermic steam reforming reaction occurs in the channels #19 through #28. Because channels #11 through #18 are interlaced with channels #19 through #28, the heat generated in #11 through #18 are transferred effectively to channels #19 through #28. This interlacing of the channels that enable efficient heat transfer may be one of the most novel features of the reformer design. Furthermore, this reformer is of a modular structure in that multiple units can be combined either vertically or horizontally depending on the required hydrogen production rate.

Experiments

Figure 2 shows the experimental setup schematically. The main components of the setup are (1) air compressor to supply oxygen to the reformer in the form of air, (2) syringe pump to supply methanol/water mixture, (3) the compact reformer, and (4) the temperature controller to control the operating temperature of the reformer. There are three pressure gauges to monitor the pressure at three different locations. The flow meter is a small volume rotameter to monitor the flow rate of the air.

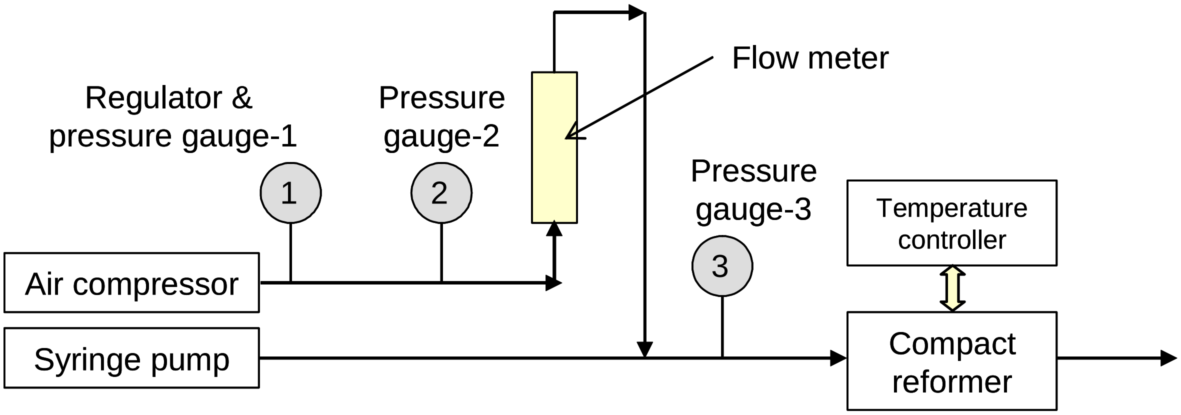

Figure 2 Schematic of the experimental Setup

The liquid-phase reactants fed by the syringe pump are methanol and water, and their molar ratio is 2.2 to 1 that is determined by the requirement that the reformer is self-sustainable meaning that the heat released by the CPOX reaction balances with the heat required by the steam reforming reaction. Thus, methanol-to-water ratio was fixed at 2.2 for all experiment whereas the oxygen feed rate was varied. In Table 1, the measured flow rate of output gas and its composition analyzed by a gas chromatography are given.

Table 1. Product gas flow rate and composition (rxn temp = 250°C; feed rate of methanol = 0.102 mol/h, water = 0.046 mol/h)

No.	Oxygen feed rate (mol/h)	Product gas flow rate (mol/h)	Product gas composition		
			CO_2	CO	H_2
1	0.037	0.48	29.7%	1.1%	69.2%
2	0.055	0.53	30.7%	0.8%	68.5%
3	0.083	0.57	32.7%	0.8%	66.5%

In all three experiments, the methanol conversion was complete whereas the conversion of water was 59% for experiment-1 and 0% for the rest.

In Table 2, theoretical predictions for the product gas flow rates and the composition are given for comparison. For these predictions, it has been assumed that only the steam reforming and the CPOX reactions are taking place without the side reaction. Thus, CO is not present in the product gas. It has been also assumed that the CPOX reaction is dominant over the SR reaction so that methanol is consumed by the CPOX reaction first until the oxygen is depleted. Thus, for experiment 3, in which the oxygen feed rate was excessive as 0.083 mol/h, all methanol is consumed by the CPOX reaction. The gas composition is a nitrogen-free composition as the gas chromatography is not set to detect nitrogen.

Table 2. Predicted value of the product gas flow rate and composition (rxn temp = 250°C; feed rate of liquid-phase reactants = 0.148 mol/h)

No.	Oxygen feed rate (mol/h)	*Product gas flow rate (mol/h)	*Product gas composition		
			CO_2	CO	H_2
1	0.037	0.47	30.6%	-	69.4%
2	0.055	0.51	33.3%	-	66.7%
3	0.083	0.57	33.3%	-	66.7%

*Predicted values

Comparison of the data in Tables 1 and 2 indicates reasonable agreement between predicted values and measured values.

Conclusion

A new idea for a compact reformer for portable PEMFC applications has been introduced. This reformer is a conventional type single-path tubular reactor packed with granular catalyst particles in which steam reforming and catalytic partial oxidation reactions take place in series. The novel feature of this reformer is in the interlacing of the flow path for efficient heat transfer between the reactor sections where the endothermic steam reforming reaction and the exothermic partial oxidation reaction are taking place respectively. Experiments using a commercial catalyst (CuO/ZnO/Al2O3) showed an excellent conversion of methanol feed and theoretical predictions appear to be in good agreement with experimental observations.

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