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# Hydrogen production with integrated microchannel fuel processor using methanol for portable fuel cell systems

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## Abstract

Microchannel methanol steam reformer was developed as compact hydrogen supplier for small fuel cells. Two types of reactors comprising fuel vaporizer, heat exchanger, catalytic combustor and steam reformer were integrated and their hydrogen production performance was evaluated. Each basic unit reactor consists of microchannel patterned stainless sheets. Methanol steam reformer was fabricated by coating a commercially available $Cu/ZnO/Al_2O_3$ catalyst inside the microchannel reactor. $Pt/Al_2O_3$ pellets prepared by incipient wetness method were filled in the cavities of the catalytic combustor. The prepared unit reactors were integrated to have independent two flow paths including catalytic combustor and methanol steam reformer for the supply of reaction heat and for the production of hydrogen, respectively. The comparison of two types of integrated reactors revealed that the fabrication process of reactor such as microchannel patterning, catalyst coating and microchannel bonding can significantly affect the reactor performance. In this work, the superior fuel processor, which has the dimensions of 60 mm × 40 mm × 30 mm, produced 450 ml/min dry reformate including 73.3% $H_2$, 24.5% $CO_2$ and 2.2% CO at 250 °C which can produce power output of 59 W.

*Keywords:* Microchannel reactor; Portable fuel cells; Hydrogen production; Fuel processor; Methanol steam reformer; Methanol combustor

## 1. Introduction

Small size polymer electrolyte membrane fuel cells (PEMFCs) would be an attractive power source for portable electronic devices. In order to power multi-functional portable devices of the future, fuel cells can be a strong candidate for replacing batteries. However, there are still significant technical barriers in developing small PEMFCs. One of the technical challenges for the systems is the development of a small size and light weight hydrogen supplying system. Hence, several systems including metal hydrides, chemical hydrides and hydrocarbon fuel reformers have been investigated as small size hydrogen suppliers. Among them, fuel reformation processors have received a great attention because of their high energy density and instant recharge time of liquid fuel. However, conventional fuel processors have too high reactor volume to be applied to small PEMFCs. Thus, microchannel reactor has been employed to minimize the chemical reactor volume mainly due to its advantages for chemical reactions such as high surface area-to-volume ratio and low linear dimensions enhancing heat and mass transfer in the reactor [1]. There are several kinds of hydrocarbon fuels as potential hydrogen sources for PEMFC systems. Among them methanol is an attractive fuel for the small fuel processor because of its low reforming temperatures, low steam to carbon ratio, good miscibility with water and low content of sulfur compounds [2].

Many efforts have been made to develop the compact and efficient microchannel methanol steam reformer for portable PEMFC applications. Pacific Northwest National Laboratory (PNNL) demonstrated 40 W equivalent microchannel fuel processor made of stainless steel which consisted of a vaporizer, steam reformer and recuperative heat exchanger [3]. Recently, they also reported sub-watt class methanol processors showing high thermal efficiencies up to 33% and low carbon monoxide emission less than 100 ppm [4]. Motorola labs disclosed integrated fuel cell system with ceramic-based

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methanol processor comprising fuel vaporizer, heat exchanger, reformer and catalytic combustor. The system was operated for 1 week generating 0.7 W electrical power [5]. Reuse et al. have fabricated an integrated fuel processor with methanol steam reformer and methanol combustor employing two independent passages using microstructured stainless steel plates. Kinetic models for steam reforming and complete combustion were also investigated in the microchannel reactor [6]. CASIO is also developing multi-layered microchannel reactor integrated with methanol reformer, CO remover, vaporizer and catalytic combustor made of glass for 10 W class PEMFC system for laptop PC [7].

Although several efforts have been made to develop the micro-scale hydrogen supplier for small PEMFC, the approach was different for each case and the research works were not clearly disclosed. This study focuses on our research processes for developing the fuel processor including microchannel patterning, basic unit of reactor fabrication, catalyst coating to microchannel reactor, reactor integration and the performance of integrated reactor. We developed two types of integrated reactors with different microchannel design, reactor integration and catalyst coating and evaluated their hydrogen generation performance. Based on these results the research guide for efficient micro-reactor was made.

## 2. Experimental

### 2.1. Fabrication and integration of microchannel reactor

We prepared two types of integrated microchannel reactors for the methanol steam reformation employing different microchannel sheet design, fabrication and integration method. Both reactors used stainless steel sheet patterned microchannel by a wet chemical etching. The microchannel shape and dimension were decided by computer simulation of flow distribution and pressure drop of the reactants in the microchannel sheet. The microchannel sheets of the reformer and combustor were coated with the respective catalysts to facilitate the appropriate chemical reactions. The prepared microchannel sheets were stacked to make basic reactors such as evaporator, heat exchanger, reformer and combustor. Finally, the basic microchannel reactors were integrated to build self-heated methanol steam reformer for PEM fuel cells. To make high performance integrated reactor, the basic reactors should be designed considering heat balance and flow distribution in the integrated reactor. Details of two integrated microchannel reactors are as follows.

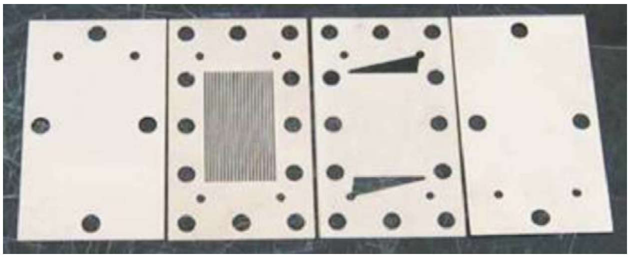

Fig. 1. Microchannel sheets for the integrated reactor A: bottom sheet, microchannel sheet, manifold sheet, cover sheet (from left).

#### 2.1.1. Integrated microchannel reactor A

Fig. 1 shows microchannel plates for integrated reactor A consisting of four types of patterned sheets including bottom sheet, microchannel sheet, manifold sheet and cover sheet. A basic unit of microchannel plate is formed by stacking the four sheets made of a stainless steel 200 μm thick. Cover sheet, bottom sheet and manifold sheets have two holes for flow path. Two triangular manifolds in the manifold sheet are fabricated to enhance the uniform flow distribution of each microchannel. A microchannel sheet also has four holes for flow path and 20 parallel channels of a rectangular shape on it. The microchannels are 500 μm wide, 200 μm deep and 33 μm long. The present microchannel design enables us to control the aspect ratio and manifold dimension of the channel by changing the number of microchannel sheets stacked. Based on preliminary studies on the combination of the sheets, the configuration of a base microchannel structure was optimized by employing a cover sheet and bottom sheet, three manifold sheets and three microchannel sheets making 600 μm deep microchannel.

A commercial $Cu/ZnO/Al_2O_3$ catalyst was used for steam reforming of methanol. The catalyst slurry for reformer was made of ICI Synetix 33-5 catalyst, 20 wt.% alumina sol (NYACOL® AL20DW colloidal alumina, PQ Corporation), distilled water and 2-propanol. In order to enhance the adhesion between catalyst powders and the substrate structure, alumina was undercoated on the surface of microchannel and then the suspension of powdered catalysts was coated on the preformed alumina layer. After drying in air, catalyst-coated metal structure was calcined at 350–400 °C. About 0.1 g of the reformer catalyst was coated on each microchannel basic structure. Hence, 0.3 g of the catalyst was equipped in the stacked microchannel reformer.

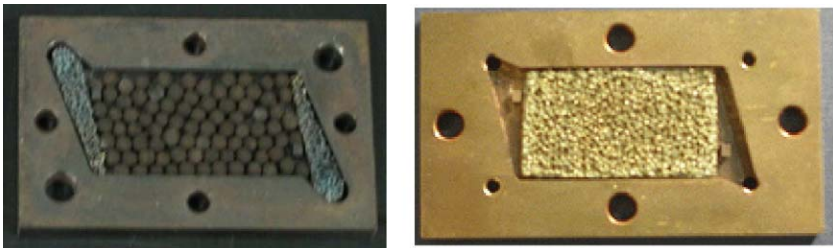

Fig. 2. Catalytic combustor filled with $Pt/Al_2O_3$ pellets (right) and $Pt/Al_2O_3$-coated Ni foam.

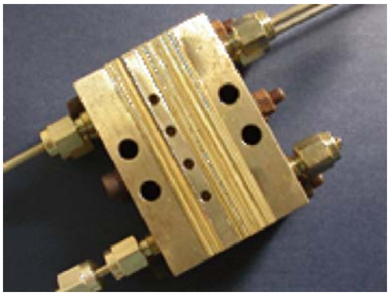

Fig. 3. Methanol fuel processor A integrated with fuel vaporizer, heat exchanger, methanol steam reformer and catalytic combustor.

A catalytic combustor was prepared by filling $Pt/Al_2O_3$-coated Ni foam or $Pt/Al_2O_3$ pellet into the cavity reactor as shown in Fig. 2. The $Pt/Al_2O_3$ combustion catalyst was synthesized by coating 5 wt.% Pt on the granular $Al_2O_3$ by incipient wetness method. About 1 g of pellet-type $Pt/Al_2O_3$ catalyst was filled in the catalytic combustor.

The microchannel vaporizer and heat exchanger was prepared by stacking base microchannel structures. The basic microchannel reactors including fuel vaporizer, heat exchanger, methanol steam reformer and methanol combustor were stacked and pressed by two end-plates for housing. The assembling method of patterned metal plates and basic reactors is similar to that of Rouge et al. [7]. The dimensions of the integrated reactor A excluding fittings were about 70 mm × 40 mm × 25 mm, respectively. Fig. 3 shows the integrated microchannel reactor. Both sides of end-plates have two holes for rod-type electric heaters, respectively.

### 2.1.2. Integrated microchannel reactor B

Fig. 4 shows another structure of microchannel sheet for integrated microchannel reactor B. In this case single microchannel patterned sheet 500 μm thick could replace the four patterned sheets for reactor A as shown in Fig. 1. Two different types of patterned plates with mirror image were prepared for two separate flow paths including reforming and combustion reactions. A manifold plate has two holes for flow path and two triangular manifolds for uniform distribution of flow through each microchannel. The plate has 34 straight microchannels which are 300 μm wide, 200 μm deep and 34 mm long as revealed in Fig. 4. The microchannel sheets were stacked and bonded by brazing process to make basic reactors such as fuel vaporizer, heat exchanger, reformer and combustor as shown in Fig. 5. It was expected that the microchannel bonding can enhance the catalytic reaction inside the channel and heat transfer between the microchannel sheets.

Methanol steam reforming reactor was also coated with reforming catalyst. To enhance the catalyst coating strength on the stainless steel sheet, the microchannel sheets were precoated with alumina. The alumina was uniformly coated on the sheet with average thickness of 20 μm as shown in Fig. 6. After alumina coating process the alumina-coated sheets were stacked and bonded by brazing process to increase the catalytic reactor capacity. Then a commercial $Cu/ZnO/Al_2O_3$ catalyst (ICI Synetix 33-5) was coated inside the microchannel stack by slurry coating method. The catalyst slurry was prepared by the same method as that used for the reactor A. About 20 mg of the catalyst was coated on each microchannel plate. Hence, the total amount of catalyst coated in the stacked reformer was 300 mg. A catalytic combustor same as that used for the integrated reactor A was used.

The fabricated basic reactors were stacked together to make an integrated fuel processor with independent two passages of reformer and combustor as shown in Fig. 7. The stacked reactors were tightened by end-plates to prevent the leak and

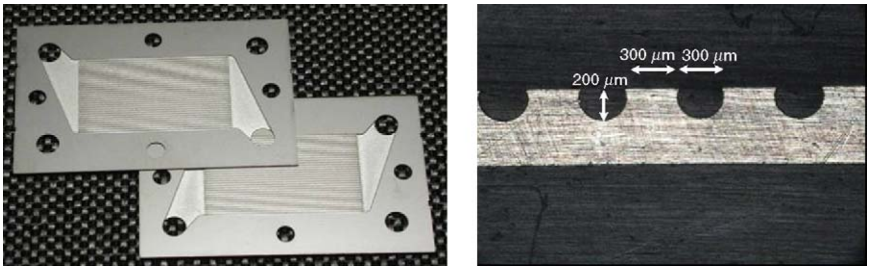

Fig. 4. Microchannel sheets for the integrated reactor B (left) and cross-sectional view of the sheet (right).

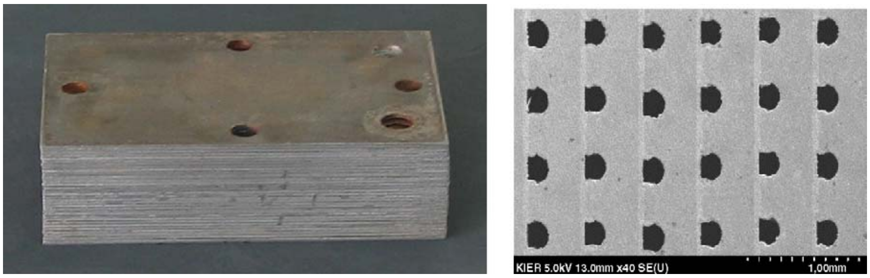

Fig. 5. Basic reactors stacked and bonded with microchannel sheets for the reactor B (left) and SEM image of cross-sectional view of the basic reactor (right).

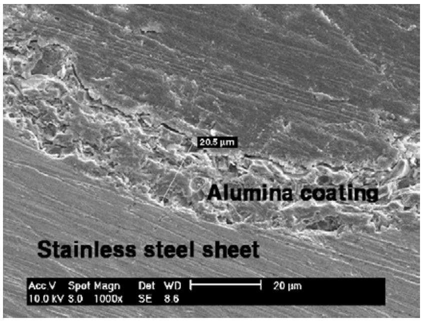

Fig. 6. SEM image of the alumina-coated microchannel sheet for the reactor B.

Fig. 7. Methanol fuel processor B integrated with fuel vaporizer, heat exchanger, methanol steam reformer and catalytic combustor.

mixing of gases between reformer and combustor. The dimensions of the integrated reactor B excluding fittings were about 70 mm × 40 mm × 20 mm, respectively.

### 2.2. Experimental set-up

The experimental apparatus consists of feed sections for steam reforming and catalytic combustion, reaction section in the integrated reactor, and the analysis section with a gas chromatograph system as shown in Fig. 8.

Methanol and water mixture was fed into the reforming reaction path of the integrated reactor by a syringe pump and methanol and air were introduced into the combustor reaction path of the reactor by syringe pump and mass flow controller, respectively.

Before the reaction the catalyst inside the reactor was fully reduced by $H_2/N_2$ stream at 230 °C for 2 h. The reactor was packed by insulation for thermal isolation. The steam reforming reaction was conducted in the temperature range 200–260 °C, which is the average temperature of the integrated reforming reactors, controlled by the electrical heater or catalytic combustor. The temperature gradient between stacked reformer plates was less than 5 °C.

The product stream was separated using a cold trap maintained at 5 °C and the flow rate of dry reformed gas was measured by a soap-bubble meter. The composition of dry reformed gas was analyzed by a gas chromatograph (Agilent 6890N) and unconverted liquid methanol was analyzed by refractometer. More details are described in our previous studies [8].

## 3. Results and discussion

### 3.1. Basic studies on reaction variables

It is well known that the methanol steam reforming reaction for hydrogen production over the $Cu/ZnO/Al_2O_3$ catalyst involves the following reactions:

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2, \qquad \Delta H^{\circ}_{298} = +49.4\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$CH_3OH \leftrightarrow CO + 2H_2, \qquad \Delta H^{\circ}_{298} = +92.0\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \qquad \Delta H^{\circ}_{298} = -41.1\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

Eq. (1) is the algebraic summation of Eqs. (2) and (3). Eq. (2) represents methanol decomposition. Eq. (3) represents a water-gas shift reaction. The major products of this process are $H_2$ and $CO_2$. Minor quantities of CO are also produced. For the application of PEMFCs, the composition of produced gas requires high concentration of $H_2$ and low concentration of CO. Hence, we studied the effect of reaction variables on the methanol steam reforming to identify the optimum operating conditions for the maximum hydrogen production with minimum CO concentration.

Methanol steam reforming was performed in the microchannel reactor A at the temperature ranges from 220 to 260 °C heated by electrically and different steam to carbon ratios of methanol–water mixtures. The feed rate of the different steam to carbon ratios of methanol–water mixtures was the same. The

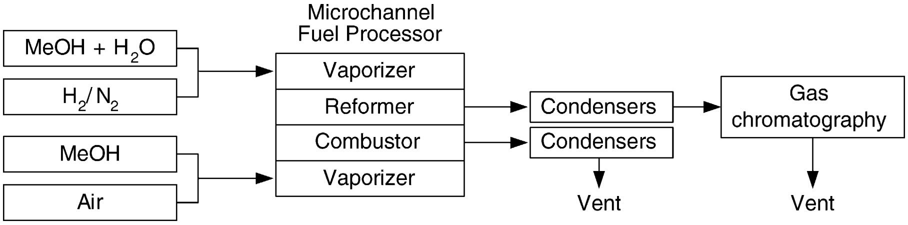

Fig. 8. Experimental set-up for microchannel fuel processor.

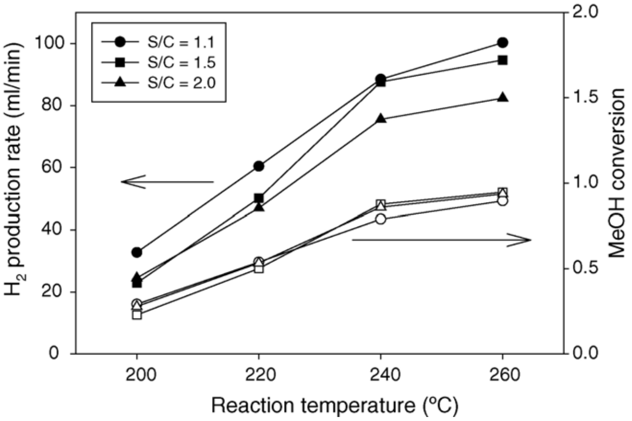

Fig. 9. Effects of reaction temperature and steam to carbon ratio on $H_2$ production (closed symbol) and methanol conversion (open symbol) in the reactor A. Reformer feed: 0.1 ml/min.

performance of the reactor is shown in Fig. 9. The $H_2$ production rate was enhanced with increasing reaction temperature. However, the amount of produced $H_2$ decreased with increasing steam to carbon ratio. This is mainly due to the decrease of absolute amount of methanol in the feed of methanol–water mixture with increasing steam to carbon ratio. Therefore, the results in Fig. 9 show that a high reaction temperature and a low steam to carbon ratio are more favorable for high amount of $H_2$ production during the methanol steam reforming.

Fig. 10 reveals the effect of reaction temperature and steam to carbon ratio on CO formation during the methanol steam reforming. The concentration of $H_2$ and $CO_2$ was less sensitive to the reaction temperature and steam to carbon ratio revealing 72–75% of $H_2$ and 24–25% of $CO_2$ at all reaction conditions. However, CO concentration increased from 0.17 to 1.6% as the reforming temperature increased from 200 to 260 °C. This is mainly because of the reverse water-gas shift reaction which is enhanced by increasing reaction temperature. The concentration of CO also decreased as the steam to carbon ratio increased. This implies that a high steam to carbon ratio can facilitate the water-gas shift reaction causing a low concentration of CO. Therefore, the reformer should be operated at a low reaction temperature and a high steam to carbon ratio to decrease the CO concentration in the reformed gas. However, the operating condition for low CO concentration is not favorable for $H_2$ production reaction. Thus, a compromise between the $H_2$ production and CO suppression is necessary for operating the reformer. For PEMFC application of the fuel processor, the CO concentration in the reformate gas should be suppressed below 10 ppm. Hence, another process should be considered to overcome the CO problem such as preferential oxidation of CO or high temperature operation of PEMFC stack.

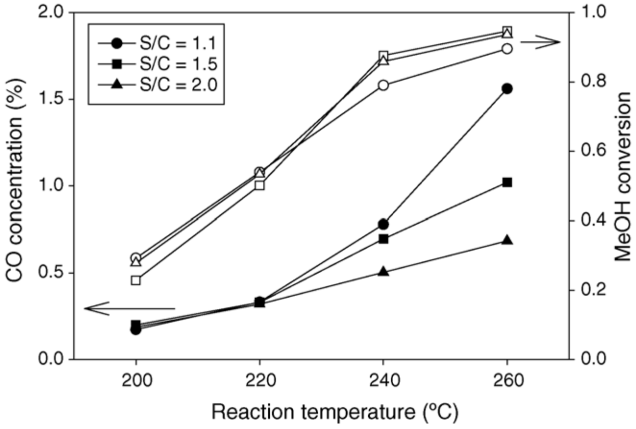

Fig. 10. Effects of reaction temperature and steam to carbon ratio on CO concentration (closed symbol) and methanol conversion (open symbol) in the reformed gas in the reactor A. Reformer feed: 0.1 ml/min.

### 3.2. *Performance of integrated microchannel reactor*

Fig. 11 shows the operating results of integrated microchannel reactor A. The reactor was heated by electrically and the electrical heater was turned off when the temperature reached to 250 °C and then methanol catalytic combustor was started to supply the heat for the reactor operation including fuel vaporization and methanol steam reforming. The results in Fig. 11 reveal that the catalytic combustor supplies enough heat for the reaction maintaining the reaction temperature around 250 °C using 0.17 ml/min of methanol as fuel. The integrated reactor A also operated for the methanol steam reforming reaction with combustion and the methanol conversion of the reformer was about 85% producing 96 ml/min of $H_2$ which amounts to the power output of 17 W. However, when the methanol–water feed into the reactor A was further increased the methanol conversion was decreased to less than 80% although the absolute amount of $H_2$ was increased. This means that the maximum capacity of the reactor A is about 17 W of $H_2$ production.

Fig. 12 shows the performance of the integrated microchannel reactor B. The reactor was started up by electrical heating up to 220 °C then the methanol catalytic combustor was started to supply the heat for the methanol reforming and fuel vaporization. When 0.2 ml/min of methanol was fed into the combustor with air, the temperature of integrated reactor steadily increased as the reaction time increases implying the combustor is supplying enough heat for all the reactions in the

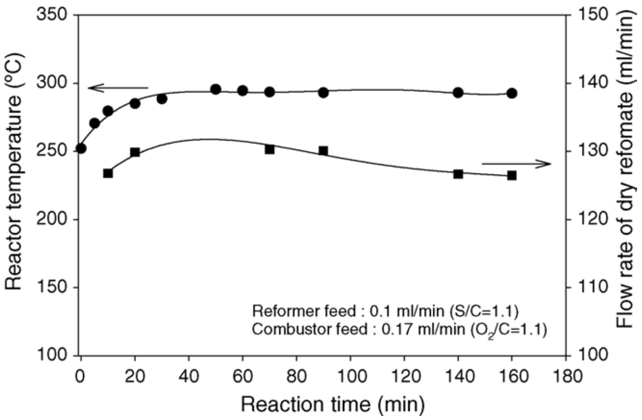

Fig. 11. Performance of the integrated fuel processor A.

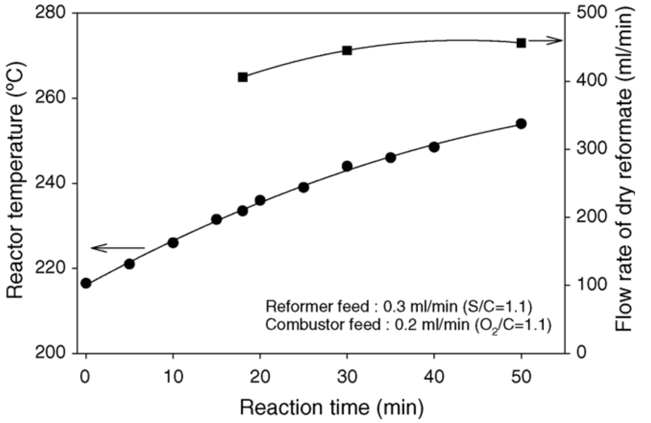

Fig. 12. Performance of the integrated fuel processor B.

Table 1
Optimum operating conditions and performance of the integrated reactors

| | Reactor type | |
|---|---|---|
| | A | B |
| Reactor temperature | 250–290 °C | 240–260 °C |
| Pressure | Atmospheric pressure | Atmospheric pressure |
| S/C (steam to carbon ratio) | 1.1 | 1.1 |
| Feed flow rate of reformer | 0.1 ml/min | 0.3 ml/min |
| Feed flow rate of combustor | 0.17 ml/min | 0.2 ml/min |
| Methanol conversion of reformer | >85% | >99% |
| Gas composition, dry basis | 73–74% $H_2$,<br>24–25% $CO_2$,<br>2–3% CO | 73–74% $H_2$,<br>24–25% $CO_2$,<br>1.6–3% CO |
| $H_2$ production rate | 0.26 mol $h^{-1}$,<br>96 sccm, 17 W | 0.88 mol $h^{-1}$,<br>330 sccm, 59 W |
| Estimated electric power (assumptions: fuel cell efficiency = 60%, $H_2$ utilization = 80%) | 8 We | 28 We |
| Integrated reactor volume | 70 $cm^3$ (70 mm × 40 mm × 25 mm) | 72 $cm^3$ (60 mm × 40 mm × 30 mm) |

integrated reactor. Hence, we operated the reformer simultaneously with the combustor and investigated the hydrogen production performance of the reactor system as a function of reaction temperature from 220 to 260 °C. More than 99% of methanol was converted at 240 °C of the reformer temperature producing about 330 ml/min of $H_2$ which amount is equivalent to the power output of 59 W. The product gas composition of the reactor revealed 73–74% $H_2$, 24–25% $CO_2$ and 1–3% CO at all reaction temperatures.

Based on the above results the optimum operating conditions and the performances of the integrated reactors were summarized in Table 1. When we compared the performances of reactor A and B, the integrated reactor B was superior to the reactor A producing three times more amount of $H_2$ at a similar total reactor volume. Although various parameters might affect the superior performance of reactor B compared to reactor A, the main factor may be the difference in reactor fabrication method. The reactor fabrication processes such as microchannel patterning, catalyst coating and microchannel bonding can affect significantly the reactor performance. These results also show that further studies should be focused on the reactor design for homogeneous flow distribution and the reactor integration for the efficient heat balance to develop more compact and high efficient integrated microchannel reactor.

## 4. Conclusions

Two types of microchannel reactors were developed integrated with the fuel vaporizer, heat exchanger, catalytic combustor and steam reformer. Each of unit reactors consists of microchannel patterned stainless sheets. Methanol steam reformer was fabricated by coating commercially available $Cu/ZnO/Al_2O_3$ catalyst inside the microchannel reactor, and the catalytic combustor was constructed by filling $Pt/Al_2O_3$ pellets inside the cavity of the reactor. The prepared basic unit reactors were integrated to have independent two flow paths including catalytic combustor and methanol steam reformer for supplying reaction heat and producing hydrogen, respectively. The comparison of the two integrated reactors revealed that reactor fabrication processes such as microchannel patterning, catalyst coating and microchannel bonding can affect significantly the reactor performance. The integrated reactor, which showed superior performance, has the dimensions of 60 mm × 40 mm × 30 mm, and produces 450 ml/min dry reformate gas including 73.3% $H_2$, 24.5% $CO_2$ and 2.2% CO at 250 °C which is equivalent to the power output of 59 W.

## Acknowledgement

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