Reaction characteristics of methanol steam reforming inside mesh microchannel reactor

Minqiang Pan a,*, Zhizhuo Feng a, Lianbo Jiang b

a School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China
b School of Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, China

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A B S T R A C T
Producing hydrogen inside microchannel reactor by reforming reaction can effectively avoid the problem of hydrogen storage for fuel cell. Compared with conventional parallel microchannel structure, mesh microchannel belongs to a kind of interconnected structure, which has been gradually applied due to its larger unit reaction area, less plugging problem, easier change and regeneration of catalyst. In this work, a mesh microchannel reactor for methanol steam reforming is developed. Comparative experiments are conducted to investigate the effects of microchannel cross-section and distribution on reaction performances under different reaction conditions. Experiment results indicate that the performance of reactor with mesh tooth microchannel plate is better than that with mesh rectangular microchannel plate. Dense-distribution in the Front direction and Sparse-distribution in the Back direction (DFSB) of both mesh tooth and rectangular microchannels present better performances than Equal-distribution in the Front-Back direction (EFB) and Sparse-distribution in the Front direction and Dense-distribution in the Back direction (SFDB) of mesh microchannels.

I N T R O D U C T I O N
Proton exchange membrane fuel cell (PEMFC) is regarded as one of the most attractive energy sources for electric vehicles due to its advantages of near zero pollution, high specific power, high energy conversion rate and low working temperature [1]. However, there are still many problems of storage and transportation of on-board hydrogen sources supplied for PEMFC, which becomes one of main obstacles for commercial application of fuel cell powered vehicle. Producing hydrogen inside microreactor on site by reforming reaction can effectively avoid the problem of hydrogen storage. Incorporation of microchannels with equivalent diameter less than 500 μm into reactor can provide high specific surface area and dramatically reduce the reactor volume. Moreover, microreactor can efficiently enhance the heat and mass transfer rate, optimize the process of complex reactions as well as improve the reaction efficiency. All these merits make producing hydrogen inside microreactor become possible to satisfy the on-site demand.

Methanol steam reforming is regarded as one of ideal methods for hydrogen production because of its advantages of low reaction temperature, high hydrogen concentration,
easy transport and storage of reactants [2,3]. Therefore, great efforts had been made on methanol steam reforming in microreactor in the past decades. Kundu et al. [4] investigated the performances of methanol steam reforming inside a microchannel reactor using stainless steel. The microreactor contained 40 parallel microchannels and each was 37 mm in length, 0.3 mm in width and 0.2 mm in depth. Results indicated that the methanol conversion could reach 99.3% and the hydrogen production rate corresponded to 1.6 W of hydrogen power could be obtained at relatively low weight hourly space velocities (WHSV). Park et al. [5] developed a micro reformer by the lamination of multiple stainless steel sheets. Each sheet was contained of 20 parallel microchannels, which length, width and depth were 33 mm, 500 μm and 200 μm, respectively. The microreactor could generate enough hydrogen for power output of 15 W. Chen et al. [6] reported a methanol reformer with 48 parallel microchannels in a stainless steel foil. Each microchannel was 30 mm long, 500 μm wide and 170 μm deep. Experimental results showed that the methanol conversion was higher than 91% at high GHSV.

It could be found from many literature [7–10] that most of the developed microreactors for methanol steam reforming were adopted parallel microchannel structure. However, it was unknown yet that whether the parallel microchannel structure was the best choice for hydrogen production. Compared with conventional parallel microchannel structure, mesh microchannel belongs to a kind of interconnected structure, which has been gradually applied due to its larger unit reaction area, less plugging problem, easier change and regeneration of catalyst. The objective of this work is to investigate the reaction characteristics of methanol steam reforming in mesh microchannel reactor. Mesh microchannel plates with two kinds of microchannel cross sections and three kinds of microchannel distributions are considered here to investigate their effects on the performances of methanol steam reforming under different GHSVs and reaction temperatures.

**Microchannel reactor structure**

**Overall microreactor structure**

As presented in Fig. 1, the microreactor for methanol steam reforming was stacked by two cover plates and two copper plates, which was sealed by graphite gaskets between them and fastened as one whole system by four bolts. The overall dimension of microreactor excluding fittings was about 85 × 85 × 40 mm³. Each cover plate was equipped with two electrical heaters to supply necessary heat for methanol steam reforming and a thermocouple was inserted into one cover plate to control the heating temperature. Two copper plates were used as the evaporation unit and reforming unit, respectively. The dimension of the copper plate was 85 mm × 85 mm × 3 mm, and a rectangular manifold with dimension of 74 mm × 39 mm × 2 mm was patterned inside the copper plate. When the copper plate was used as the reforming unit, a mesh microchannel plate coated with catalysts was loaded into the rectangular manifold for methanol steam reforming. By this way, it was convenient to change microchannel plates with different cross sections and distributions for investigating the effects on reaction performances. Moreover, two dependent plates were beneficial to the rapid processing of mesh microchannels by conventional milling process. During reaction, the mixture of methanol and water firstly flowed into the evaporation unit, in which it was heated and evaporated into gas. Then the gaseous reactant entered the reforming unit for reaction.

**Mesh microchannel plate**

In this work, the influences of microchannel cross-section and distribution on the reaction performances of methanol steam reforming were investigated. Therefore, two different microchannel cross-sections, rectangular and tooth, were adopted here. As for the distribution of mesh microchannel, only the horizontal microchannels were changed whereas the vertical microchannels maintained uniform. Three kinds of microchannel distribution in the Front-Back direction were investigated, which were Equal-distribution in the Front-Back direction (EFB), Sparse-distribution in the Front direction and Dense-distribution in the Back direction (SFDH), Dense-distribution in the Front and Sparse-distribution in the Back direction (DSFB). Here the Front-Back and Left-Right direction were defined in Fig. 2. DSFB and SFDH could be interchangeable by rotating the plate 180° horizontally.

Each mesh microchannel plate contained 22 microchannels in the Left-Right direction and 10 microchannels in the Front-Back direction. Each microchannel had the same length and cross-section area, whether rectangular or tooth cross-section. Rectangular microchannel was 1 mm in width and 1 mm in depth, and the cross-section area was 1 mm². When the depth of tooth microchannel was 1.3 mm, the cross-section area was approximately 1 mm² calculated by SEM image. The detailed parameters of each mesh microchannel plate were shown in Table 1.

The manufacture process of mesh microchannel plate was conducted on a vertical milling machine X5032, as shown in Fig. 3. In order to fabricate microchannels in longitudinal and transverse direction on the surface of metal plate, the microchannel plate was fixed on a fixture plate in two directions by fabricating multiple thread holes in the fixture plate. The parallel microchannels in longitudinal direction were firstly machined by altering the cutting height in Z direction every time when the microchannel plate was clamped in vertical direction. After finish machining the longitudinal microchannels, the transverse microchannels were then machined by changing the chamfered direction of microchannel plate. In that way, the mesh microchannels were formed.

**Experimental**

Prior to the experiment, the catalyst for methanol steam reforming was prepared. Cu(NO₃)₂, Zn(NO₃)₂, Al(NO₃)₃ and Zr(NO₃)₄ with a molar ratio of 11:6:4:1 were mixed in distilled water, in which the copper ion concentration was 4.6%. Then it was mixed with Al₂O₃ colloidal solution to form a precursor
mixture of catalyst. Al₂O₃ colloidal solution could effectively enhance the adhesive power of catalyst and microchannel plate. Zr-containing catalyst not only can increase the reducibility of copper, but also improve its decomposition capability and present higher surface area, and hence improve reaction performance [11]. The catalyst mixture was uniformly coated in the microchannel plate and then dried in an oven. All the above steps were repeated until each copy of
The precursor solution for each microchannel plate was finished. The amount of catalyst coated in each microchannel plate was 0.1 g.

After the catalyst preparation, the catalyst-coated microchannel plate and evaporation plate were assembled between two cover plates to form a microreactor. Then the catalyst inside the microchannel plate was activated by the test system as shown in Fig. 4, which was consisted of a reactant supply system, a temperature control system, a data collection and analysis system. The catalyst-coated microchannel plate was calcined at 300°C for 2 h under the protection of 80 ml min⁻¹ N₂, and then reduced for 1 h in the mixture of 80 ml min⁻¹ N₂ and 30 ml min⁻¹ H₂.

After the catalyst reduction, the protection gas was turned off and the heated temperature was adjusted to the reaction temperature for methanol steam reforming. The mixture of methanol and water in 1:1.3 M ratio supplied from fuel tank was fed into the microreactor by a syringe pump. After the reforming reaction, the unreacted methanol and moisture in the reformate was separated in a cold trap. While the reforming reaction was progressing steadily, the reformate composition was analyzed by an on-line gas chromatograph equipped with a TCD detector, and the flow rate was measured by a soap-bubble flow meter.

In this work, methanol steam reforming was conducted at two different reaction temperatures, 260°C and 300°C. The feed rate of mixture of methanol and water was varied from 1 ml h⁻¹ to 5 ml h⁻¹ with an increment of 1 ml h⁻¹. According to the amount of catalyst load inside the microchannels, the corresponding GHSV was changed from 8126 to 40,631 ml g⁻¹ h⁻¹.

**Table 1 – Detailed parameters of different mesh microchannel plates.**

<table>
<thead>
<tr>
<th>Cross-section</th>
<th>Rectangular</th>
<th>Tooth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distribution</td>
<td>EFB</td>
<td>DFSB</td>
</tr>
<tr>
<td>Dimension</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Fig. 3 – The machining device and clamping methods for milling mesh microchannels.**
The reaction performances of methanol steam reforming was evaluated by the following parameters, including methanol conversion $X_{\text{MeOH}}$, $\text{H}_2$ selectivity $S_{\text{H}_2}$, CO selectivity $S_{\text{CO}}$ and flow rate of $\text{H}_2$ $v_{\text{H}_2}$, as defined below.

$$X_{\text{MeOH}} = \frac{F(y_{\text{CO}} + y_{\text{CO}_2})}{22.4 \times v_{\text{MeOH, in}}} \times 100\%$$ (1)

$$S_{\text{H}_2} = \frac{F(3y_{\text{CO}_2} + 2y_{\text{CO}})}{v_{\text{MeOH, in}} \times X_{\text{MeOH}}} \times 100\%$$ (2)

$$S_{\text{CO}} = \frac{C_{\text{CO}}}{C_{\text{CO}_2} + C_{\text{CO}}} \times 100\%$$ (3)

$$v_{\text{H}_2} = F \times y_{\text{H}_2}$$ (4)

where $F$ was the normal flow rate of effluent gas, $y$ was the volumetric fraction, $C$ was the concentration in the reformate, $v_{\text{MeOH, in}}$ was the molar flow rate of methanol fed into the microreactor.

**Results and discussion**

**Effects of microchannel cross-section on the reaction performances**

Methanol conversion

Fig. 5 presented the effects of microchannel cross-section on methanol conversion under different GHSV's and reaction temperatures. At the same reaction temperature, it could be found that methanol conversion for all the plates with different microchannel cross-sections and distributions decreased as increased GHSV. The larger the GHSV was, the less contact time of reactant and catalyst was, which resulted in insufficient reaction and low methanol conversion. Under the same GHSV, methanol conversion increased as the increased reaction temperature from 260 °C to 300 °C. That was because methanol steam reforming belonged to a strong endothermic reaction and the reaction rate increased as the increased temperature.

It was also indicated that the methanol conversion inside the mesh tooth microchannel was at least 10% higher than that inside the mesh rectangular microchannel under the same GHSV and reaction temperature. Since the preparation process and loading method of catalyst for all the mesh microchannels were exactly the same, it could be considered that the difference of microchannel cross-section led to the difference of the catalyst activity under the same reaction condition. It was inferred that tooth cross-section was helpful for the increase of methanol conversion. The possible reason was that the tooth microchannels were helpful to increase the contact time between the reactant and catalyst since the refraction action of both slope side could increase the flow process of reactant inside the catalyst.

$\text{H}_2$ and CO selectivity

The influences of microchannel cross-section on $\text{H}_2$ and CO selectivity under different GHSV's and reaction temperatures were shown in Fig. 6. Based on the overall curve trend, it was obvious that $\text{H}_2$ and CO selectivity presented the opposite trend with the same microchannel distribution and reaction conditions. When $\text{H}_2$ selectivity reached its maximum value, CO selectivity was the minimum, and vice versa. It was also indicated that $\text{H}_2$ selectivity decreased and CO selectivity increased with the increase of reaction temperature in most case. When the reaction temperature increased, the catalyst activity increased and methanol conversion was improved. However, the amount of coated catalyst was relatively small in this experiment. More methanol occurred decomposition in insufficient reaction and low methanol conversion. Under the same GHSV, methanol conversion increased as the increased reaction temperature from 260 °C to 300 °C. That was because methanol steam reforming belonged to a strong endothermic reaction and the reaction rate increased as the increased temperature.

1-fuel tank; 2-AJ-5803 syringe pump; 3-D07 mass flow controller; 4-reactor; 5-220V electric source; 6-AL-708 temperature controller; 7-thermocouple; 8-cold trap; 9-soap-bubble flow meter; 10-6820 gas chromatograph; 11-computer

Fig. 4 – Test system for methanol steam reforming inside the microreactor.
Fig. 5 – Effects of microchannel cross-section on methanol conversion.

Fig. 6 – Effects of microchannel cross-section on H$_2$ and CO selectivity.
and reverse water-gas shift reaction. Thus the decomposition reaction and reverse water-gas shift reaction were responsible for the increase of CO selectivity. On the other hand, H₂ selectivity decreased and CO selectivity increased as GHSV increased under a certain reaction temperature. Because the GHSV was somewhat large related to the catalyst amount, some of the methanol directly flowed out of the microreactor without reaction, which greatly reduced methanol conversion and led to the decrease of H₂ selectivity and the increase of CO selectivity.

The effects of microchannel cross-section on H₂ and CO selectivity were summarized as Table 2. It was indicated from Table 2 that the mesh tooth microchannel plate presented higher H₂ selectivity and lower CO selectivity than the mesh rectangular microchannel plate in the investigated range of GHSV and reaction temperature. However, the differences of H₂ and CO selectivity between two kinds of microchannel cross-sections were less than 5%.

### H₂ production rate

Fig. 7 presented the H₂ production rate with different microchannel cross-sections in the investigated range of GHSV and reaction temperature. It was indicated that H₂ production rate increased with the increase of GHSV and reaction temperature for all kinds of microchannel distributions. On the condition of a certain amount of catalyst, the increasing GHSV meant that more methanol was entered the microreactor and occurred reforming reaction. Therefore more reformate gas was produced and led to the increase of H₂ production rate. On the other hand, methanol conversion increased due to the enhancement of catalyst activity at high reaction temperature, which also made contribution to the increase of H₂ production rate. It could also be found from Fig. 7 that the mesh tooth microchannels presented higher H₂ production rate than the mesh rectangular microchannels at the investigated operating conditions.

### H₂ and CO concentration in the reformate

Fig. 8 showed the H₂ and CO concentration with different microchannel distributions under various GHSVs and reaction temperatures. On the whole, it could be found that H₂ concentration slightly decreased as GHSV increased. Due to the decreased contact time between reactant and catalyst as GHSV increased, methanol conversion decreased and resulted in the increase of proportion of methanol in the reformate and the decrease of H₂ concentration. However, the reaction temperature showed little influences on the change of H₂ concentration. On the same reaction conditions, the H₂ concentrations of EFB and SFDB with mesh tooth microchannels were higher than that with mesh rectangular microchannels, whereas H₂ concentrations of DFSB inside two kinds of microchannel cross-sections were approached to each other.

As for CO concentration, it could be found that CO concentration increased with the increase of reaction temperature and GHSV in most case. Some work had demonstrated that CO concentration increased with the increase of reaction temperature in a traditional fixed bed reactor [12]. Thus the variation law of CO concentration with the reaction temperature in this work was the same with that in fixed bed reactor. As for the reason for the increase of CO concentration with the increasing GHSV here, it was because the increase of GHSV reduced the contact time between methanol and catalyst as well as the supplied reaction heat. Since the activation energy of methanol decomposition was lower than that of methanol steam reforming, methanol decomposition preferentially occurred in the case of insufficient heat supply, which led to the increase of CO concentration in the reformate. It could also be concluded from Fig. 8 that CO concentration of EFB and DFSB inside the mesh rectangular microchannels was higher than that inside the mesh tooth microchannels, whereas SFDB inside the mesh rectangular microchannels presented lower CO concentration than that inside mesh tooth microchannels under the same reaction temperature and GHSV.

### Effects of microchannel distribution on the reaction performances

#### Methanol conversion

As showed in Fig. 9, the highest methanol conversion of 91% was obtained at 300 °C for SFDB. In most cases, methanol conversions inside both tooth and rectangular microchannels under the same reaction temperature and GHSV from high to low were: DFSB > SFDB > EFB. The difference of methanol conversion between them with the same cross-section was less than 15%, except for mesh tooth microchannels at 260 °C.

#### H₂ and CO selectivity

Fig. 10 showed the influences of microchannel distribution on H₂ and CO selectivity. As for mesh rectangular microchannels, it could be found that H₂ and CO selectivity with various microchannel distributions were closed to each other. The differences between them were about 5%. SFDB had the highest H₂ selectivity and the lowest CO selectivity at 260 °C whereas EFB had the highest H₂ selectivity and the lowest CO selectivity at 300 °C. As for mesh tooth microchannels, the effects of microchannel distribution on H₂ and CO selectivity were more obvious. Under the same GHSV and reaction temperature, the sequence of H₂ selectivity from high to low was that: EFB > DFSB > SFDB. It could be figured out that EFB got the highest H₂ selectivity and lowest CO selectivity in most cases.

#### H₂ production rate

The effects of microchannel distribution on the H₂ production rate were shown in Fig. 11. On the whole, the highest H₂ production rate could be reached 0.173 mol h⁻¹. Whether

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### Table 2 – Effects of microchannel cross-section on H₂ and CO selectivity.

<table>
<thead>
<tr>
<th>Microchannel distribution</th>
<th>Reaction temperature (°C)</th>
<th>Higher H₂ selectivity</th>
<th>Lower CO selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) EFB</td>
<td>260</td>
<td>Tooth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>Tooth</td>
<td></td>
</tr>
<tr>
<td>(b) SFDB</td>
<td>260</td>
<td>Tooth</td>
<td>Rectangular</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>Tooth</td>
<td>Rectangular</td>
</tr>
<tr>
<td>(c) DFSB</td>
<td>260</td>
<td>Tooth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>Tooth</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7 – Effects of microchannel cross-section on the H₂ production rate.

Fig. 8 – Effects of microchannel cross-section on H₂ and CO concentration.
mesh rectangular or tooth microchannels, H₂ production rate under the same reaction conditions in descending order was as follows: DFSB > SFDB > EFB. It could be concluded that the microreactors with non-uniformly distributed microchannels in the Front-Back direction had higher H₂ production rate than that microchannels of equal distribution. On the other hand, the difference of H₂ production rate among different microchannel distributions decreased with the increased reaction
H2 and CO concentration in the reformate

Under the same reaction conditions, the differences of H2 concentration among various mesh rectangular microchannels were quite obvious, as presented in Fig. 12(a). H2 concentrations were arranged from high to low as follows: DFSB > EFB > SFDB. As for mesh tooth microchannels, the differences of H2 concentration were quite small, as shown in Fig. 12(b). H2 concentrations in mesh tooth microchannels were ranked from high to low as: SFDB > EFB > DFSB.

As showed in Fig. 13(a), CO concentrations inside the mesh rectangular microchannels under the same GHSV and reaction temperature from high to low were: DFSB > EFB > SFDB. As presented in Fig. 13(b), CO concentrations inside mesh tooth microchannels were arranged from high to low as follows: SFDB > DFSB > EFB. It was obvious that the difference of microchannel cross-section led to different CO concentration with the same microchannel distribution.

Statistical analysis of comprehensive reaction performances

Analysis under different microchannel cross-sections

Table 3 presented the comprehensive performance comparison of microchannel cross-sections. It could be found that EFB with mesh tooth microchannels had better performance than that with mesh rectangular microchannels at both 260°C and 300°C. The performance of DFSB at 300°C with mesh tooth microchannels was better than that with mesh rectangular microchannels. For DFSB and SFDB at 260°C, mesh rectangular microchannels presented better performance in some cases, while the others mesh tooth microchannel did. Generally, mesh tooth microchannels presented better comprehensive reaction performances than mesh rectangular microchannels.

Analysis under different microchannel distributions

The comprehensive performance of microreactors with different microchannel distributions was presented as Table 4. It could be found that it was hard to know which one presented the best performance. According to the rankings of each performance indicator, the best was scored 3 points and
the worst was scored 1 point. Therefore Table 4 was transformed into histograms, as shown in Fig. 14, and afterwards Fig. 14 was summarized as Table 5. It was indicated that DFSB presented the best performance with mesh rectangular microchannel at 300 °C and mesh tooth microchannel at both 260 °C and 300 °C.

Conclusions

In this work, a mesh microchannel reactor used for methanol steam reforming is developed. In the reforming unit, microchannel plates with two kinds of microchannel cross-sections and three kinds of microchannel distributions are selected. Comparative experiments are conducted to investigate the reaction performances under different GHSVs and reaction temperatures. The performance indicators include methanol conversion, $\text{H}_2$, and CO selectivity, $\text{H}_2$ production rate, $\text{H}_2$ and CO concentration in the reformate. According to the ratings of the investigated performance indicators in the experiments, statistical analysis of comprehensive reaction performances of all microchannel cross-sections and distributions are carried out. The results indicate that reaction performance with mesh tooth microchannels is better than that with mesh rectangular microchannels. On the other hand, DFSB presents better performances of methanol steam reforming than SFDB.
and EFB. Although DFSB has the best comprehensive performance, some works still have to be done to optimize the structure in further study.

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References


Fig. 14 – Performance comparison of three kinds of microchannel distributions.

| Table 5 – Performance comparison of three kinds of microchannel distributions. |
|-------------------------|----------------------|----------------------|
| Microchannel cross-section | Reaction temperature (°C) | Performance comparison |
| Rectangular | 260 | SFDB > DFSB > EFB |
| | 300 | DFSB > SFDB = EFB |
| Tooth | 260 | DFSB > EFB > SFDB |
| | 300 | DFSB > EFB > SFDB |