

High efficiency and low carbon monoxide micro-scale methanol processors

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Abstract

A micro-scale power supply is being developed to provide an alternative to current secondary batteries for use in microelectronics devices, such as microsensors. The work discussed in this paper expands on this earlier reported sub-watt power generation system. Two designs were evaluated: a processor optimized to improve the thermal efficiency of the methanol reforming reactor from 9 to above 20%, and a system tailored to decrease the carbon monoxide levels to below 500 ppm, preferably lower than 100 ppm. Each design was operated over a range of feed flow rates. Thermal efficiencies up to 33% were demonstrated with the optimized processor, likely as a result of the low operating temperature, high methanol concentration (~60 wt.%) in the feed, and the high hydrogen production. Up to 3.55 scfm hydrogen was produced with relatively low carbon monoxide. In the second design, significant decreases in carbon monoxide, in some cases below 100 ppm, were achieved while maintaining reasonable thermal efficiencies of up to 19%.

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1. Introduction

In recent years, there has been considerable interest in the development of miniature sub-watt electric power generation using hydrocarbon fuels [1–9]. This research mainly focused on creating a power supply with greater energy density than the secondary batteries currently in microelectronic devices, such as microelectromechanical systems (MEMS) and microsensors. Due to the high energy density of hydrocarbons (e.g., methanol ~5.6 kWh/kg compared to lithium-ion batteries ~0.12 kWh/kg), even a very inefficient chemical to electrical energy conversion device could be a significant improvement over the available secondary battery technology [9]. The new technologies range from thermal electric generators embedded in micro-scale combustors to silicon-based MEMS rotary engines [4,6].

In previous papers, we reported the development of a sub-watt power generation system based on a micro-scale methanol processor and a miniature fuel cell [9,10]. The micro-scale processor described previously consisted of two vaporizers, a heat exchanger, a catalytic combustor and a methanol reformer [9]. The methanol reformer reactor was less than 5 mm³. The total volume of this device was less

than 0.2 cm³, with a weight of less than 1 g, and could be operated without any external heating. The product gas was composed of 73–74% hydrogen, 25–26% carbon dioxide, and the remainder carbon monoxide. The thermal efficiency was calculated to be approximately 9% by dividing the lower heating value of the product hydrogen by the lower heating value of the methanol fed to the reformer and the fuel fed to the combustor (Eq. (1)):

$$\text{Efficiency} = \frac{\Delta H_c \text{Hydrogen}_{\text{produced}}}{\Delta H_c \text{Methanol}_{\text{feed}} + \Delta H_c \text{Fuel}_{\text{feed}}} \quad (1)$$

The major limitation on the thermal efficiency was heat loss due, primarily, to conduction. For a reactor of this small this size, the performance was notable; however, improvements in efficiency and a significant lowering of the carbon monoxide would greatly increase the device's viability.

This paper discusses the performance of two next-generation micro-scale methanol processors. The first processor consisted of an optimized design to improve the thermal efficiency of the methanol reforming reactor from 9 to above 20%. The second design investigated the possibility of decreasing the carbon monoxide levels from the originally reported 1–2% to below 500 ppm, preferably lower than 100 ppm.

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Fig. 1. Second generation micro-scale fuel processor—high efficiency.

2. Experimental

2.1. High thermal efficiency micro-scale methanol processor

The fuel processor, Fig. 1, was composed of the same unit operations as the earlier device. This second generation processor was constructed of 316 stainless steel, but could also be built of high-temperature ceramics. The fabrication, assembly, and testing were all performed in-house. The combustor had a volume of less than 5 mm³, the reformer had a volume of less than 50 mm³, and the fuel processor had a volume of less than 0.2 cm³ with a mass of less than 1 g. Proprietary catalysts developed in-house were used in both the catalytic combustor and reformer. The reformer feed was a methanol–water mixture with a 1:1.2 molar ratio (~60 wt.% methanol). A 0.01 in. thermocouple was inserted into the combustion reactor to monitor the device operation temperature. Liquid fuel was fed using syringe pumps at rates from 0.03 to 0.2 cc/hr (20 °C basis). At these low flow rates the average flow was consistent, but slight variations of flow (pulsing) were observed. The combustion fuel was either methanol or hydrogen. Between 10 and 25 sccm air was fed to the combustor, depending on the needed reactor temperatures. After water vapor was removed from the reformat, using Dri-rite, the product gases were analyzed with an on-line micro gas chromatograph (Agilent QuadH).

Table 1
Fuel processor performance at >99% methanol conversion

Feed rate (cc/hr)	<i>T</i> (°C)	Reformat flow (sccm)	Hydrogen (%)	Carbon monoxide (%)	Carbon dioxide (%)	Thermal efficiency (%)
0.05	255	1.2	73–74	0.4–0.6	25–26	15
0.08	263	2.0	73–74	0.5–0.7	24–26	21
0.12	270	3.0	73–74	0.5–0.6	25–26	25
0.15	280	3.8	72–73	0.6–0.7	25–27	28
0.18	313	4.5	72–73	0.8–1.0	25–26	30
0.20	320	4.9	72–73	1.0–1.1	25–26	33
Original Processor [9]						
0.05	400	1.1	73–74	1.0–2.0	25–26	9



Fig. 2. Second generation micro-scale fuel processor with CO removal reactor (right) with the high efficiency reactor (left) for comparison.

2.2. Carbon monoxide reduction

The carbon monoxide was removed by selectively reacting it with hydrogen to form methane. A separate reactor was added to the fuel processor for the methanation step (Fig. 2). The reactor was built of 316 SS and had a volume of less than 0.1 cm³. The total volume of the processor plus methanation reactor was less than 0.3 cm³ and still weighed less than 1 g. A proprietary selective carbon monoxide methanation catalyst was fabricated in-house. The

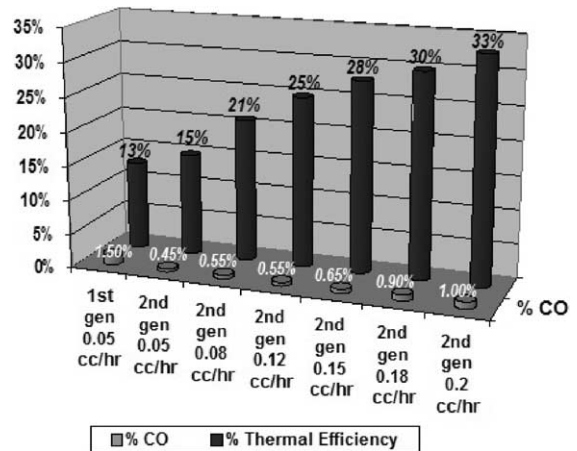


Fig. 3. High efficiency reactor performance.

Table 2
Methanol processor with integrated carbon monoxide removal reactor performance

Feed rate (cc/hr)	T ($^{\circ}\text{C}$)	Reformate flow (sccm)	Hydrogen (%)	Carbon monoxide (ppm)	Carbon dioxide (%)	Methane (%)	Thermal efficiency (%)
0.05	304	1.0	69–70	<100	25–25.5	5.0–5.5	9.5
0.08	323	1.65	69–70	<200	25–25.5	6.0–6.2	14
0.10	330	2.1	69–70	<200	25–25.5	6.0–6.2	17
0.15	345	3.2	68–69	<300	25–26	5.3–6.0	19

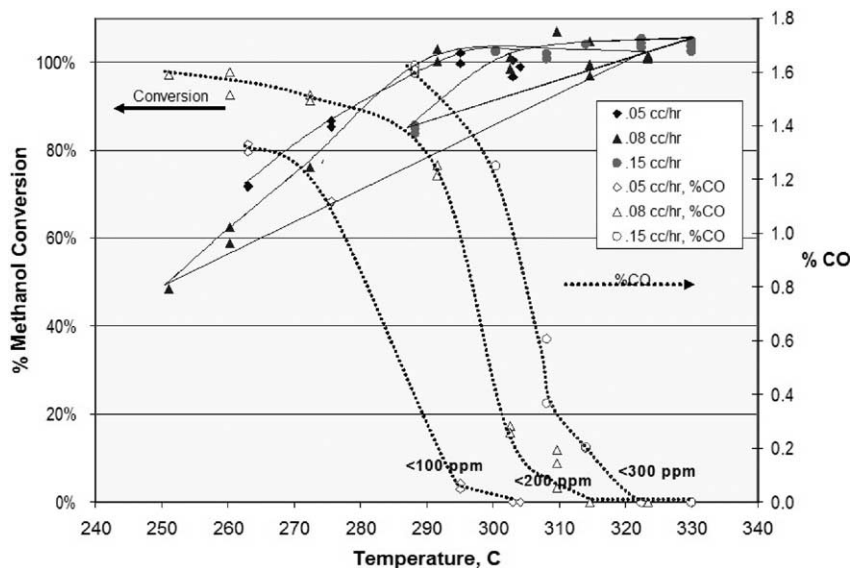


Fig. 4. Low carbon monoxide fuel processor performance.¹

completed system was composed of six unit operations: two vaporizers, a heat exchanger, a catalytic combustor, a steam reformer, and a methanation reactor. The liquid feeds, gas feeds, and product gas analysis were the same as above. The low carbon monoxide was measured using an infrared gas analyzer (ZRH, California Analytic Instruments).

3. Results and discussion

3.1. High thermal efficiency micro-scale methanol processor

The reactor was operated over a wide range of feed flow, i.e., 0.05–0.2 cc/hr. Table 1 and Fig. 3 summarize of the reactor performance.

At similar feed rates, the new design achieved >99% methanol conversion at significantly lower temperature. The conversion was calculated by performing a carbon balance on the effluent. The capacity of the device was increased by a factor of 4, while still maintaining low temperatures. Low methanol reforming temperatures favor the production of carbon dioxide over carbon monoxide, which was evident in these data.

High thermal efficiencies from 15 to over 30% were achieved. The high efficiencies were ascribed to the lower operating temperatures, the low steam to carbon ratio of

1.2:1 compared to 1.8:1, and the higher capacity. The lower operating temperatures significantly decreased thermal losses, leading to higher efficiencies. The low steam to carbon ratio decreased the amount of water that needed to be vaporized and heated, decreasing the heat duty. Finally, the thermal efficiency increased with higher production as expected. In other words, the thermal losses as a percentage of the thermal power of the hydrogen produced should decrease with increased power.

3.2. Carbon monoxide reduction

The integrated fuel processor/carbon monoxide methanation reactor was operated with feed rates from 0.05 to 0.15 cc/hr. Higher operation temperatures were required to achieve >99% methanol conversion. It was also observed that the carbon monoxide levels did not decrease until >95% conversion was achieved. It is hypothesized that methanol decomposes on the methanation catalyst, thus producing methane, carbon dioxide and carbon monoxide. Table 2 and Fig. 4 summarize the results.¹

Carbon monoxide reduction was achieved at all flow rates, with <100 ppm CO being achieved at flow rates of

¹ Conversion >100% was sometimes calculated when the carbon did not balance. This calculation was attributed to experimental error and slight variations in flow (pulsing) from the pumps, which was observed.

0.05 cc/hr. However, a significant decrease in thermal efficiency also occurred. The efficiency loss was caused by higher operating temperatures and also a loss of hydrogen to methane and water from the carbon monoxide cleanup reactors. The methane levels indicate that some carbon monoxide was being methanated in addition to the carbon monoxide. It is estimated that approximately 13–15% of the hydrogen was consumed in the methanation reactor, much higher than the anticipated 7–10%. The high methane production was likely due to methanator operation at higher than ideal temperatures (220–270 °C) for selective carbon monoxide methanation. A reactor model is being developed to determine the temperature distribution and also to optimize the design.

4. Conclusions

A micro-scale power supply is being developed to power microelectronics such as microsensors. A miniature methanol fuel processor that has thermal efficiencies up to 33% has been demonstrated. It is believed that the low operating temperature, high methanol concentration (~60 wt.%) in the feed, and the high hydrogen production contributed to the thermal efficiency. The fuel processor was able to produce up to 3.55 sccm hydrogen with relatively low carbon monoxide. For use with conventional fuel cell technology a catalytic carbon monoxide cleanup reactor was integrated onto the fuel processor. Significant decreases in carbon monoxide, in some cases below 100 ppm, were achieved while maintaining reasonable thermal efficiencies of up to 19%.

Acknowledgements

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