

Microfuel processor for use in a miniature power supply

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Received 25 September 2001; accepted 13 November 2001

Abstract

A microscale fuel reformer for use with a miniature fuel cell has been built and operated at efficiencies that make them attractive for use as a miniature power supply for microelectronics. The fuel reformer and the results of initial tests are discussed. The fuel processor assembly consists of two vaporizer/preheaters, a heat exchanger, a combustor, and a steam reformer. Methanol was identified as a good candidate for use in the microscale reformer. A proprietary catalyst was developed to reform methanol. The catalyst was able to process a methanol water mixture (1:1 by weight) into a hydrogen-rich stream composed of 73–74 vol% H₂, 25–26 vol% CO₂, and 0.6–1.2 vol% CO on a dry basis. Almost 3 mols of hydrogen per mol of methanol reacted, which approached the theoretical maximum. An integrated fuel processor that used proprietary catalyst in the reformer and catalytic combustion to provide the heat was designed and built. The reformer and combustor were each less than 5 mm³ in volume. When 100 mW_e of hydrogen was produced, a thermal efficiency of 9%, or an estimated 4.5% net efficiency (including a hypothetical fuel cell), was achieved. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fuel reformer; Microscale power; Microdevice; MEMS; Fuel cell; Hydrogen generation

1. Introduction

Supplying power to microelectronic devices for remote and autonomous operation has proven to be a formidable challenge [1,2], as current battery technology does not provide the energy densities needed to sustain power for extended periods. Even lithium-ion battery technology can only produce an energy density of 0.15 kW_e h/kg, and, while expected to achieve 0.2 kW_e h/kg in the next few years [3], Li-ion still will not come close to the potential energy densities that can be reached through thermal conversion of hydrocarbon fuels. Table 1 shows a comparison of current practical battery technology and expected future energy densities.

In this paper, a miniature power supply technology is described that is based on hydrocarbon fuel sources. This technology, being developed by Battelle Pacific Northwest Division (Battelle) and Case Western Reserve University (CWRU), combines a miniature fuel cell (1–2 cm²) with a micro hydrocarbon fuel reformer. Since hydrocarbons have much higher energy densities than batteries (e.g. 5.6 kW_t h/kg for methanol and 12.6 kW_t h/kg for butane), converting

the thermal energy in hydrocarbons to electricity with efficiencies even as low as 5% would result in devices with energy densities equivalent to current Li-ion batteries. The technology discussed here is targeting efficiencies of 5% or greater using hydrocarbon fuel sources. This paper concentrates on the fuel reformer, which incorporates Battelle's technology advancements in microchemical and thermal systems [5–12]. Tests were conducted with various catalysts, and the best suited catalyst was selected for testing in an engineered system with methanol as the hydrocarbon fuel.

2. Fuel processor overview

A typical fuel processor is composed of five unit operations: fuel vaporizers/preheaters, fuel reformers, clean-up (carbon monoxide) unit(s), heat exchangers (recuperators), and combustor. Pumps, blowers, valves, insulation and other miscellaneous peripheral devices are needed to feed the fuel, water, air, and to ensure the device operates properly. Fig. 1 is a schematic of a representative system.

2.1. Fuel reformer

The heart of a fuel processor system is the fuel reformer, which is a catalytic reactor where the hydrogen is stripped

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Table 1
Current practical battery technology [4] and hydrocarbon energy densities

Technology	Energy density (kW _e h/l)	Energy density (kW _e h/kg)	Comments
Primary cells	–	–	Not rechargeable
Alkaline	0.330	0.125	–
Zn–air	1.050	0.340	–
Li/SOCl ₂	0.700	0.320	–
Secondary cells	–	–	Rechargeable
Lead acid	0.070	0.035	–
Ni–cad	0.055	0.035	–
Ni–metal hydride	0.175	0.050	–
Li–ion	0.200	0.120	–
Li–polymer	0.350	0.200	Anticipated
Hydrocarbons			
Methanol	4.384	5.6	Thermal energy
Butane	7.290	12.60	Thermal energy
<i>Iso</i> -octane	8.680	12.34	Thermal energy

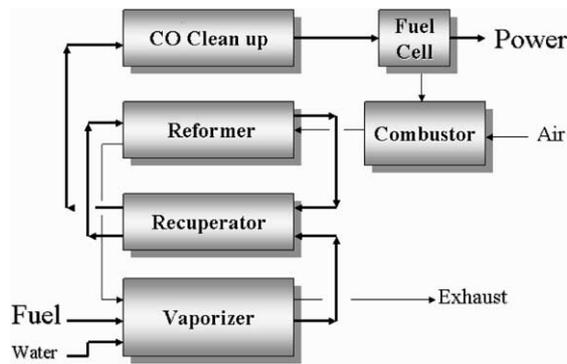
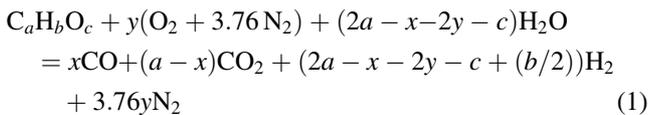


Fig. 1. Fuel processor schematic.

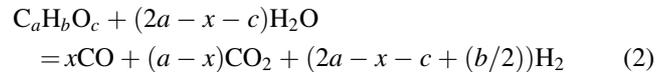
from a hydrocarbon fuel. A general fuel processing equation is:



Where the specific equation is dependent on the fuel type and the reforming technology.

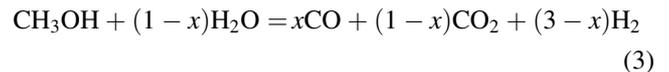
Typical reforming technologies for processing hydrocarbon fuels include partial or preferential oxidation, autothermal reformation, and steam reforming [13]. Both preferential oxidation and autothermal reformation intro-

duce oxygen (air) into the system and burn with the reforming fuel to produce the heat required for the reforming reaction(s) to occur. In steam reforming, an external combustor is used to provide the heat. While each technology has advantages and disadvantages [13], steam reforming was applied in this work because it offers the highest theoretical efficiency and provides the highest hydrogen composition. These conditions may improve fuel cell performance in the product gas stream (reformat) compared with preferential oxidation and autothermal reforming [13,14]. With the reforming technology selected, we can simplify Eq. (1) so it is only dependent on the fuel type:



For a miniature power supply, all the water needed for the reforming would likely be carried on the system. The water weight should therefore be included in the energy calculation of the hydrocarbons, as depicted in Table 2. For comparison purposes, the ideal minimum amount of water required for the hydrocarbon conversion was used in these calculations. The methanol water mixture has an energy density greater than that of the other hydrocarbon/water mixtures.

Methanol was selected for the initial testing because it reformed at the lowest temperatures. The reforming temperature is important since the heat loss from such a small device is considerable. With methanol selected as the fuel, the reforming reaction can be further simplified to Eq. (3):



From the above reaction, it is clear that to maximize the hydrogen production, the carbon monoxide production must be minimized. If no carbon monoxide is produced, the molar ratio of hydrogen produced to methanol fed to the reactor would be 3:1. Carbon monoxide removal is discussed in Section 2.2.

2.2. Reformate clean-up

The reformat stream is composed of hydrogen, carbon dioxide, and carbon monoxide. Fuel cells operate best on pure hydrogen, but can tolerate carbon dioxide and some other gases such as nitrogen. However, the typical PEM fuel cell can tolerate only 10–20 ppm carbon monoxide [15].

Table 2
Fuel processor feed energy density (hydrocarbon + water)

Fuel	Steam to carbon ratio	Energy (kW _t h/l)	Energy (kW _t h/kg)	Reforming temperature (°C)
Methanol	1	2.810	3.290	300–400
<i>n</i> -Butane	2	2.570	3.110	450–650
<i>n</i> -Octane (gasoline)	2	2.670	2.990	550–750

Consequently, researchers are looking at ways to produce PEM fuel cells with a higher CO tolerance [15,16]. While CWRU has developed a fuel cell that can tolerate up to 5 vol% CO in their hydrogen feed stream, which reduces the clean-up requirements of the reformat stream significantly, for proper fuel cell operation, the carbon monoxide levels in the reformat stream still must be lower than 5 vol% [17]. Typically this clean-up is accomplished in one of two ways. The first method is a multi-step process consisting of water gas shift reactors, combined with selective oxidation and/or carbon monoxide methanation [13]. The second clean-up method is through the use of a hydrogen-permeable membrane [13].

3. Experimental results and discussion

Screening tests were conducted to determine which catalyst formulation would offer the best performance for the system. The selected catalyst was then engineered into an integrated steam reformer unit, and a second set of tests was performed to determine the efficiency of the engineered unit.

3.1. Catalyst screening tests

The key component of the reformer reactor is the catalyst. Battelle has developed novel ways of engineering catalyst monoliths that allow high mass transfer rates at a

low pressure drop [18]. The catalyst supports are specially engineered foam supports from pure metals, alloyed metals, or ceramics. The foams have a very high porosity (10–100 pores/inch) and large pore sizes (<200 μm), which provide the high mass transfer rates. For more conventional catalytic systems, mass transfer is the rate-limiting step, so relatively large devices are required to maximize throughput, and high activity catalysts are not required. By using Battelle's engineered catalyst monoliths, high activity catalysts can be used to assemble much smaller devices that are capable of maintaining comparable processing rates.

In addition, Battelle has developed its own proprietary catalyst for methanol reforming. All catalysts were fabricated in house. The catalyst was tested over a temperature range of 250–450 °C. Distilled de-ionized water was added to the fuel to make a mixture with the desired molar ratio of steam to carbon. The first test was to determine an optimal steam to carbon ratio for methanol processing. The catalysts were tested over a range of molar steam to carbon ratio from 3:1 to pure methanol, and a contact time (CT) of approximately 100 ms, except for the flow of pure methanol (Fig. 2). The reforming temperature of 360 °C at a steam to carbon ratio of 1.8:1 was found to be the lowest temperature required to obtain >99% conversion. No significant change in the reformat composition was observed. The multiple contact times were also tested to determine the effect of longer contact on the reaction. As expected, with an increase in contact time, the temperature required to

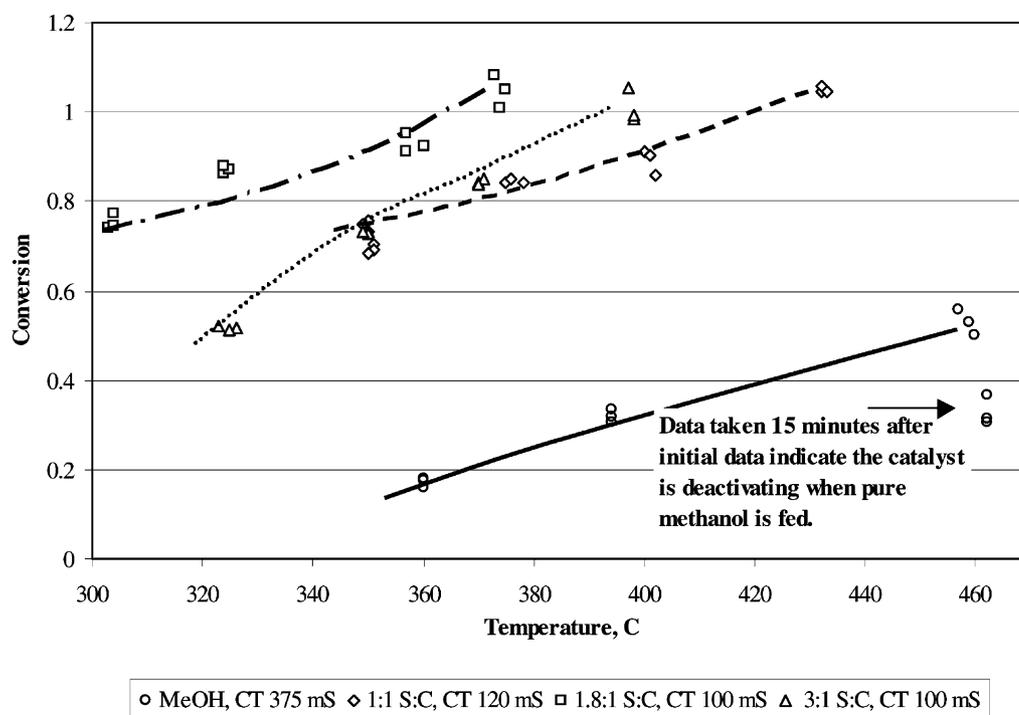


Fig. 2. Effect of steam to carbon ratio on the catalyst performance. The steam to carbon ratio of 1.8:1 appeared to give the best results. (See footnote 2).

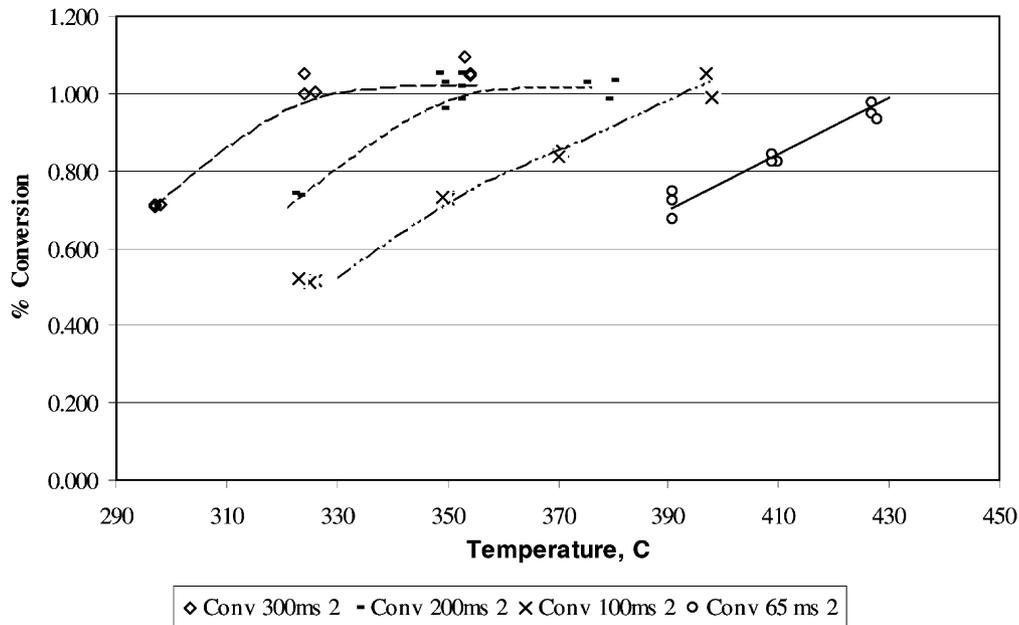


Fig. 3. Effect of contact time on methanol reforming. As expected, longer contact times allowed lower processing temperatures. (See footnote 2).

achieve >99% conversion also decreased (Fig. 3). The conversion was calculated by doing a carbon balance on the effluent.¹

A commercial catalyst (Cu/Zn on alumina) was also tested for comparison. Under identical conditions, steam to carbon ratio of 1.8:1 and contact time of 300 ms, the Battelle catalyst was able to convert >99% of the methanol fed to the reactor at a lower temperature of 320 °C compared to 420 °C required to achieve >99% methanol conversion with the commercial catalyst (Fig. 4). As well as requiring higher temperatures to obtain >99% conversion, the reformat of the commercial catalyst had much higher CO levels than that from the Battelle catalyst (Table 3). During the tests, the commercial catalyst produced approximately 2 mols hydrogen for each mol of methanol reacted. In contrast, the reformat from the Battelle catalyst had a significantly higher percentage of hydrogen, a lower percentage of carbon monoxide, and no methane produced.² Furthermore, the Battelle catalyst resulted in 2.7–2.8 mols of hydrogen produced for each mol methanol reacted, which approaches the ideal of 3 mols as calculated from Eq. (3). This higher purity of hydrogen results in superior fuel cell performance over lower purity hydrogen.

3.2. Integrated fuel reformer system

The integrated fuel processor test system was built in house and was composed of five unit operations: two

vaporizers/preheaters, a reformer, catalytic combustor, and heat exchanger (Fig. 5). The device was built of 316 stainless steel, but could also be built of high temperature ceramics. The fabrication, assembly and testing were all done in house. The heat for liquid vaporization, gas preheating, and for the reforming reaction(s) was provided by catalytic combustion of hydrogen or methanol. Both the reformer and the combustor had volumes less than 5 mm³. The reformer had a capacity of 200 mW_t, while the combustor had a capacity of up to 3 W_t. The oversized combustor capacity allowed a wide range of operating conditions to be examined, and a thermal couple was inserted into the combustor to monitor the device temperature. The total device volume was less than 0.2 cm³. Calculations indicated that a temperature difference between the combustor and steam reformer would be only a couple of °C, which is within the error of the thermocouple.

The system was mounted inside a larger tube for testing. The larger tube provided support to the extremely thin inlet and outlet tubes to the device. Additional equipment was connected to the test stand, including syringe pumps, gas

Table 3

Typical reformat dry gas composition from the Battelle catalyst and Cu/Zn catalysts with water + methanol (S:C 1.8:1) as fuel

Gas	Battelle catalyst (%)	Cu/Zn on alumina
Hydrogen (H ₂)	73–74	65.9%
Carbon dioxide (CO ₂)	25–26	22.5%
Carbon monoxide (CO)	0.6–1.2	3.1%
Methane (CH ₄)	0.0	8.5%
Mols H ₂ /mols methanol reacted	2.7–2.8	2.0

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

² Methane is produced by the reaction: $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$.

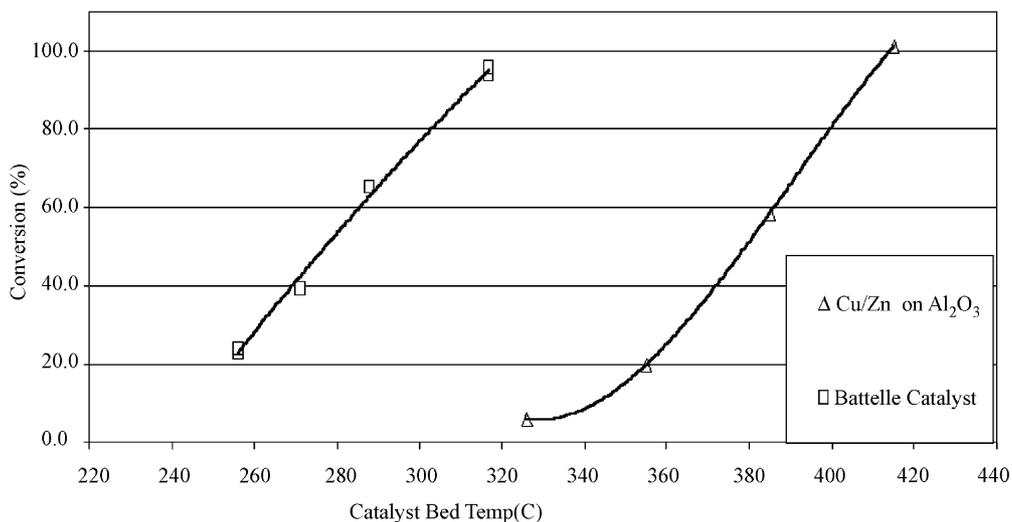


Fig. 4. Comparison of the Battelle catalyst with Cu/Zn on alumina (commercial) catalyst at steam to carbon ratio of 1.8:1 and 300 ms contact time. Lower temperature was required to achieve >99% methanol conversion on the Battelle catalyst compared to the commercial catalyst tested.

controllers, vapor liquid separation units, and an on-line gas chromatograph (Fig. 6). The methanol water mixture was fed to the reformer via syringe pumps at rates of 0.02–0.1 cm³/h (20 °C basis), and pure methanol to the combustor at rates of 0.1–0.4 cm³/h (20 °C basis). About 8–20 sccm of air were fed to the combustor, depending on the reaction conditions. The product reformat gases were fed to an on-line micro gaschromatograph (Agilent QuadH), via a dri-rite tube, which eliminated any water vapor.

The reformer was operated over a wide range of conditions. To achieve >99% conversion, operating temperatures greater than 400 °C in the combustor were required. These temperatures were higher than anticipated, and were attributed to the internal flow patterns, faster contact times than used in the catalyst screening tests, and thermal losses to the environment.

The thermal efficiency was calculated by dividing the lower heating value of the hydrogen in the reformat stream

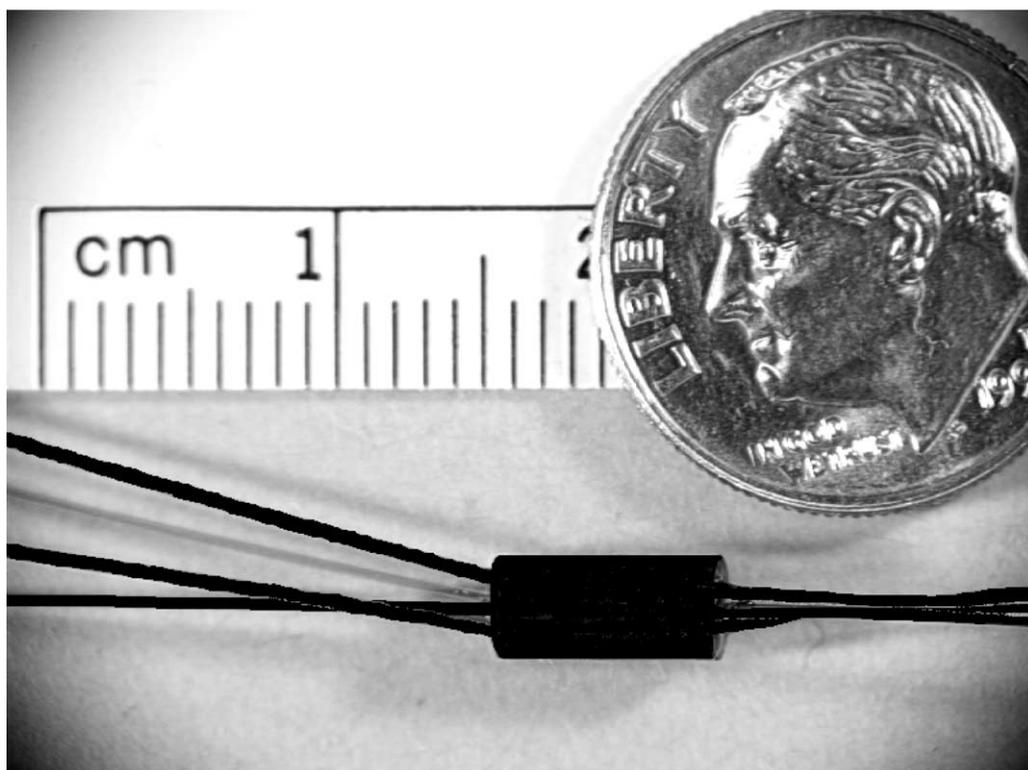


Fig. 5. Integrated fuel processor system.

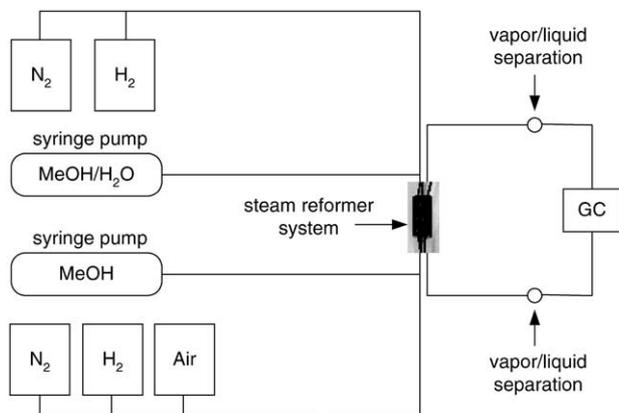


Fig. 6. Testing equipment schematic.

by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor (Eq. (4)).

$$\text{Efficiency} = \frac{\Delta H_c \text{ hydrogen}}{\Delta H_c \text{ reformer} + \text{combustor methanol feed}} \quad (4)$$

Where ΔH_c is the lower heat of combustion of hydrogen or methanol as indicated.

The 200 mW_t power was achieved with a thermal efficiency of 9%. As the reformer output was decreased, the efficiency also decreased. For example, when the reformer produced 70 mW_t, the efficiency decreased to 6%. This result was expected since the thermal losses as a percent of the total amount of power fed to the device increases as the size is decreased.

The anticipated electrical power from a fuel cell powered by this stream can be found by multiplying the thermal power by the net fuel cell efficiency. Typical fuel cells operate at 60% efficiency and utilize 80–85% of the H₂ in a reformat stream for a net efficiency of $\approx 50\%$. Thus, it is anticipated that a fuel cell utilizing the reformat from this device could provide ≈ 100 mW_e, and the system (reformer + fuel cell) would have an estimated net efficiency of $\approx 4.5\%$.

In theory, the efficiency of the system could be improved by feeding the unreacted hydrogen from the fuel cell back to the combustor. Yet, the resultant net efficiency would be 4.7%, only a slight increase from the original, assuming no additional heat loss due to the extra manifolding required to recycle the hydrogen. This small increase in efficiency is not sufficient to make such integration appealing, especially since, in reality, the recycle manifolding would most likely increase the heat loss of the system. Instead, an improved design will more likely provide the efficiency desired. Since the system was operated at temperatures close to the reforming temperature of some hydrocarbons, designing an improved system will include the feasibility of reforming higher hydrocarbons.

4. Summary and conclusions

A high-energy power supply is being developed that provides more extended operating times and efficiencies for microelectronic devices than conventional battery technologies. An integrated methanol fuel reformer system has been designed and built. Screening tests were first conducted to determine the best catalyst performance for the reformer. The results from the catalyst testing showed that the Battelle catalyst was superior to the commercial catalyst tested for comparison, Cu/Zn on alumina. Initial testing of the engineered fuel reformer system resulted in the production of 200 mW_t of hydrogen at a high efficiency of 9% utilizing methanol as fuel. The reformat stream was composed of 73–74% hydrogen, with 25–26% carbon dioxide and carbon monoxide constituting the rest. The device approached the ideal conversion ratio of 3 mols hydrogen produced per mol of methanol reacted. A complete system would consist of liquid and gas delivery systems, valves, packaging, and integration with a fuel cell.

Acknowledgements

This work was supported in part by Defence Advanced Research Projects Agency contract # DABT63-99-C-0039. Their support is gratefully acknowledged.

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