High-efficiency microscale power using a fuel processor and fuel cell

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ABSTRACT

A microscale power device, composed of a fuel processor and a fuel cell, is described, and results of testing conducted with the fuel reformer are presented. The microscale fuel reformer strips hydrogen from a hydrocarbon fuel, such as methanol, and the hydrogen-rich stream can then be fed to a fuel cell to generate electrical power. In the tests discussed here, the fuel reformer, utilizing methanol, was able to provide up to 100 mW_e of hydrogen at an efficiency of up to 4.8%. The device was able to operate independent of any additional external heating, even during start-up.

Keywords: fuel reformer, microscale power, micro device, MEMS, fuel cell, hydrogen

1. INTRODUCTION

The conventional battery technology typically used in microelectronic devices and microelectromechanical systems (MEMS) is insufficient to provide the energy these systems require, especially compared with the potential of high-power, high-energy, microscale systems that utilize hydrocarbon fuels. Table 1 is an overview of energy densities available with typical practical battery technology. As shown in the table, lithium-ion (Li-ion) batteries currently have an energy density of 0.15 kW_e-hr/kg. While Li-ion batteries are expected to achieve 0.2 kW_e-hr/kg in the next few years,[1] they still cannot reach the energy densities possible with microscale devices, which ma y eventually be >0.5 kW_e-hr/kg.

Table 1. Current practical battery technology[2]

Technology	Energy Density, Whr/L	Energy Density, kW_e-hr/kg	Comments
Primary Cells			Not rechargeable
Alkaline	330	0.125	
Zn-air	1050	0.340	
Li/SOCl$_2$	700	0.320	
Secondary Cells			Rechargeable
Lead acid	70	0.035	
Ni-cad	55	0.035	
Ni-metal hydride	175	0.050	
Li-ion	200	0.150	
Li-polymer	350	0.200	Anticipated

As an alternative to conventional batteries, Battelle Pacific Northwest Division (Battelle) and Case Western Reserve University (CWRU) are developing a power supply that combines a small fuel cell with a micro hydrocarbon fuel reformer. Since hydrocarbons have much higher energy densities than batteries (5.6 kW_t-hr/kg for methanol and 13.2 kW_t-hr/kg for diesel), even an inefficient (2%) conversion of the thermal energy in hydrocarbons to electricity would result in devices with equivalent energy densities of current Li-ion batteries. The technology being developed here is based on a targeted 5% or greater conversion. Transforming thermal energy to electricity is achieved by stripping the hydrogen from the hydrocarbon fuel (called reforming) and converting it in a proton exchange membrane fuel cell

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(PEMFC). Battelle's role in this technology centers on the fuel processor, and this paper focuses on the design of the fuel reformer and the results of initial testing.

Battelle is a leader in the development of miniature reactors[3-6] and recently won two R&D 100 awards from *Research and Development Magazine* (1999), in addition to holding patents.[7, 8] Battelle's Micro Chemical and Thermal Systems (MicroCats) program has developed and applied this technology to miniature chemical reactors, heat exchangers, and other chemical and physical processes, as well as equipment with characteristic dimensions on the micrometer scale. Figure 1 illustrates the different characteristic size ranges for different applications. Research is now underway to implement MicroCat technology in portable fuel processors[3,9] (0.1 mW_e to 25 mW_e), compact fuel processors[10] (automotive uses), high efficiency compact heat exchangers/vaporizers,[8] and space exploration[4] (in-situ propellant generation and life support systems), in addition to the application discussed here.   Some advantages of this technology are listed below:

- Lightweight and compact
- Rapid heat and mass transfer in the device, which allows the use of extremely active catalysts
- Extremely precise control of process conditions (e.g., temperature)
- High performance devices (allow high throughput in small devices)
- Competitive cost through mass production
- Possible integration of multiple unit operations in small volumes
- Distributed and portable devices in applications that were traditionally stationary (hand-held chemical plants).
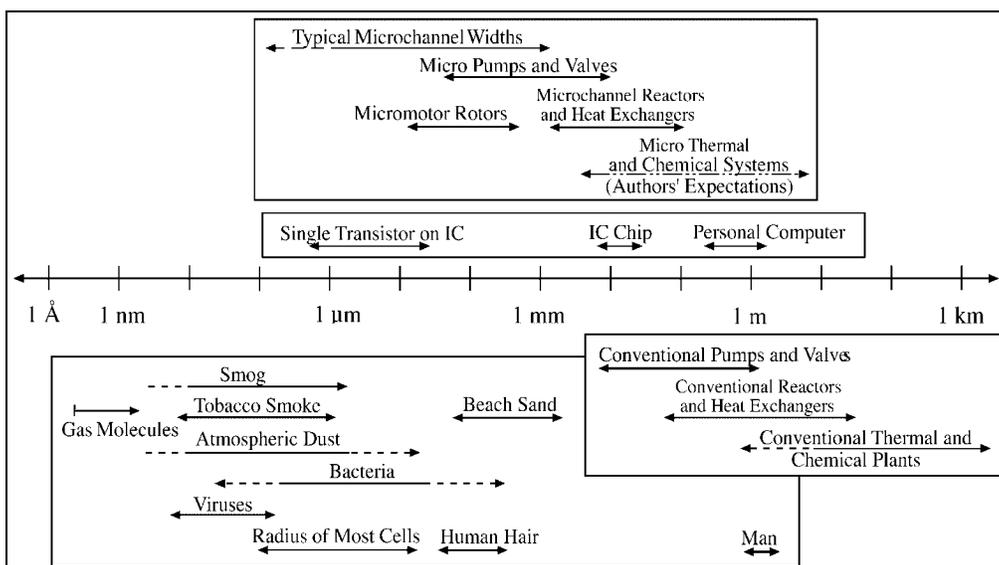

Figure 1. Characteristic sizes of common systems

2. PROCESS DESCRIPTION

A typical fuel processor is composed of five significant unit operations: fuel vaporizers/preheaters, fuel reformers, fuel clean-up unit(s), heat exchangers, and combustor. Additional components include pumps, blowers, valves, insulation, and other peripheral devices. Figure 2 shows a schematic of a representative system.
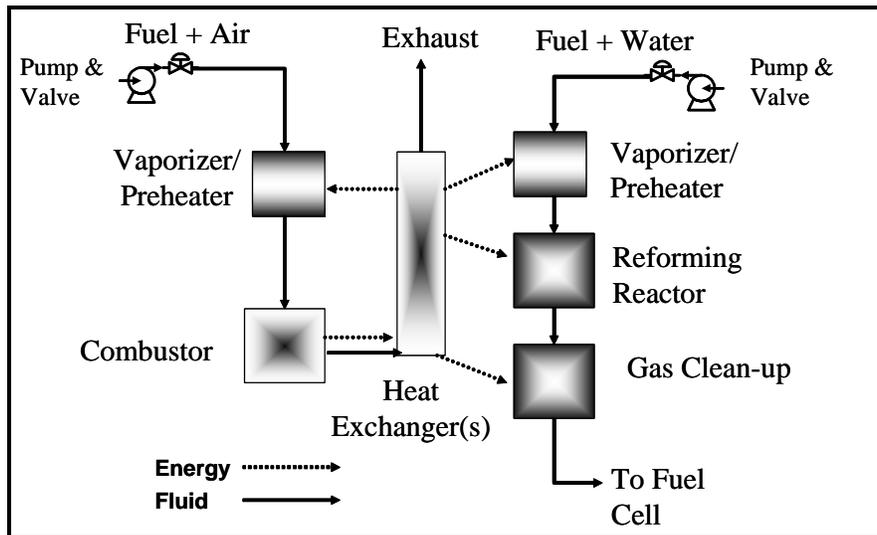
Figure 2. Fuel processor schematic

2.1 Fuel reformer

The heart of the system is the fuel reformer, a catalytic reactor where the hydrogen is stripped from a hydrocarbon fuel. Technologies used to process the hydrocarbon fuels include partial or preferential oxidation, autothermal reformation, and steam reforming.[11] In preferential oxidation and autothermal reformation, oxygen (air) is introduced into the system and burned with hydrogen 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,[11] in this work, steam reforming was applied since it offers the highest theoretical efficiency and provides the highest hydrogen composition in the product gas stream (reformate),[11,12] which may improve fuel cell performance.

2.2 Reformate clean-up

The reformate stream is composed of hydrogen, carbon dioxide, and carbon monoxide. PEMFCs operate best on pure hydrogen, but can tolerate carbon dioxide and some other gases, such as nitrogen. However, the typical fuel cell can only tolerate a limited amount of carbon monoxide (10 – 20 ppm).[13] Work on PEM fuel cells with a higher carbon monoxide tolerance is underway.[13,14] CWRU has developed fuel cell that can tolerate up to 5 vol% CO in their hydrogen feed stream, which eases the clean-up requirements of the reformate stream significantly.

The carbon monoxide levels can be decreased through two different methods. The first method is a multi-step process consisting of water-gas shift reactors, combined with selective oxidation and/or carbon monoxide methanation.[11] The second method uses a hydrogen-permeable membrane, which allows only hydrogen to diffuse through it, to make a pure (>99.99%) hydrogen stream, effectively removing any CO or CO_2.[11]

2.3 Combustor and heat exchangers

Heat must be provided to the system to vaporize/preheat the fuel and provide the environment for the reforming reactions. In steam reforming, this heat is typically provided by burning a small amount of hydrocarbon fuel mixed with any hydrogen gas that is not reacted in the fuel cell. The combustor exhaust is fed to the heat exchangers to direct the heat to the areas needed. This thermal integration is the key to achieving a feasible, let alone efficient, device.

2.4 Other components

Other essential constituents for the system include pumps, valves, blowers (fans), tanks, insulation, controls, and packaging. For efficient operation, passive liquid delivery systems (0.03 ml/hr – 0.2 ml/hr), gas delivery systems (5 sccm – 20 sccm), valves, and controls would be ideal. These components are not being investigated at this time, but we believe many can be operated passively after an initial expenditure of energy to begin the processes.

2. EXPERIMENTAL RESULTS AND DISCUSSION

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

3.1 Catalyst screening tests

Catalyst monoliths developed at Battelle allow high mass transfer rates at low ΔP's.[15] These 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. In this case, however, high activity catalysts can be used to assemble much smaller devices that are capable of maintaining comparable processing rates.

Two catalyst categories were examined. The first category was catalysts that could process a wide range of fuels (from methanol to diesel). The catalysts were tested over a temperature range of 350°C to 650°C. Water was added to the fuel to make a mixture with a 3:1 molar ratio of steam to carbon. The results of the experiments with the best catalyst are presented in Figure 3. High processing rates at relatively low temperatures were attained. For the initial device, methanol was selected as the fuel of choice. From these initial designs and tests, second-generation devices operating on higher hydrocarbon fuels (e.g., butane) will be developed.
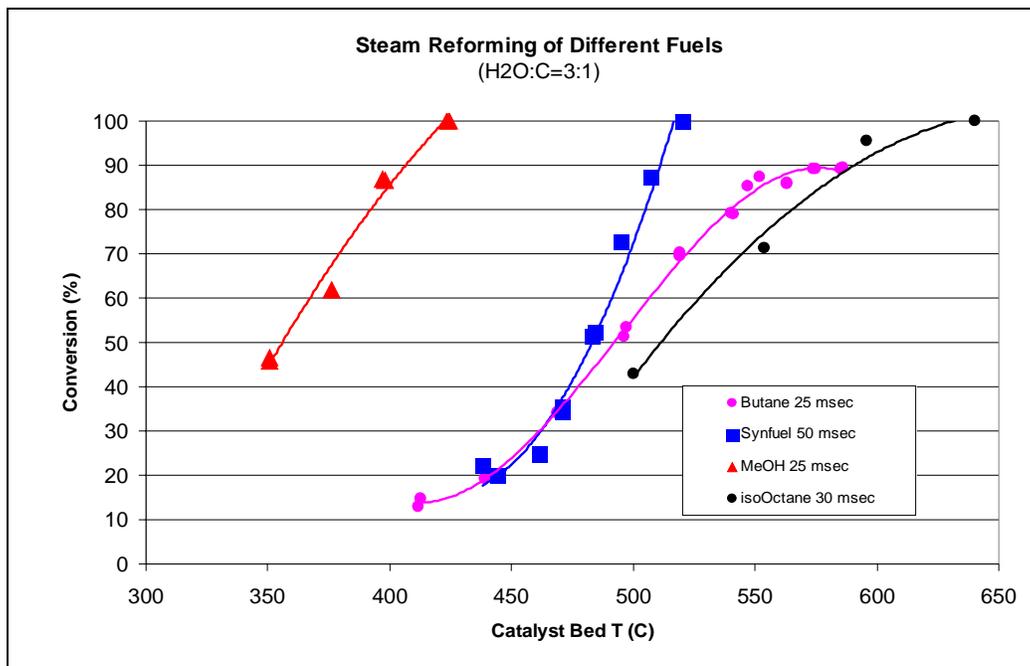

Figure 3. Multi-fuel catalyst screening test

Additional catalysts developed specifically for methanol were also tested (see Figure 4). These catalysts were tested with a molar steam to carbon ratio of 1.8:1. The Cu/Zn catalyst on alumina is a commercially available catalyst that was tested for comparison purposes. The catalysts developed at Battelle exhibited performance at least equal to the commercial catalyst. Catalyst F was able to react 100% of the methanol at the lowest temperature ($\approx$300°C). In addition to the reformation temperature, carbon monoxide production was examined. Catalyst F also produced the lowest amount

of carbon monoxide (≈ 1 vol%). Figure 5 shows the catalyst selectivity to react carbon in the methanol to carbon monoxide as opposed to other carbon compounds (e.g., carbon dioxide). Zero or near zero selectivity to carbon monoxide is desired. Typical dry gas composition for the reformate of catalyst F is given in Table 2. Unlike most PEM fuel cells, the CWRU fuel cells can tolerate this level of carbon monoxide. Therefore, combining CWRU's fuel cell technology with a fuel-processing device utilizing this catalyst would eliminate the need for a clean-up unit operation — greatly simplifying the overall system and reducing the system size.
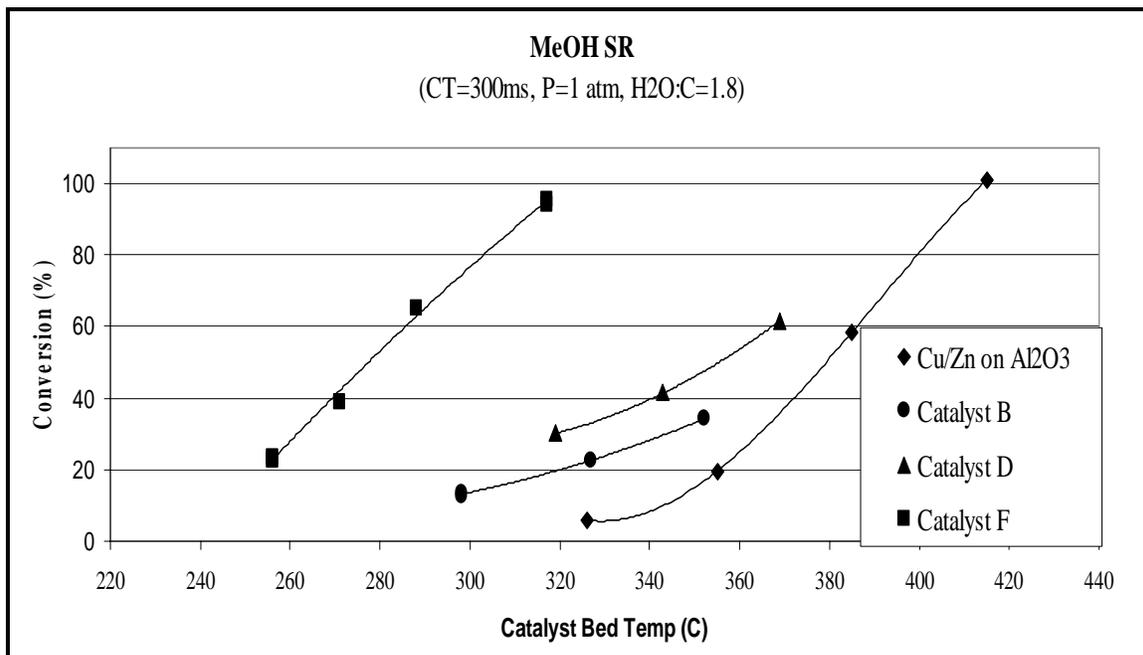
MeOH SR
(CT=300ms, P=1 atm, H2O:C=1.8)

Figure 4. Methanol catalyst screening results at 1 atm pressure, contact time = 300 ms, and a 1.8:1 steam to carbon ratio

MeOH SR-CO Selectivity vs Temperature
(CT=100ms, H2O:C=1.8, P= 1 atm)
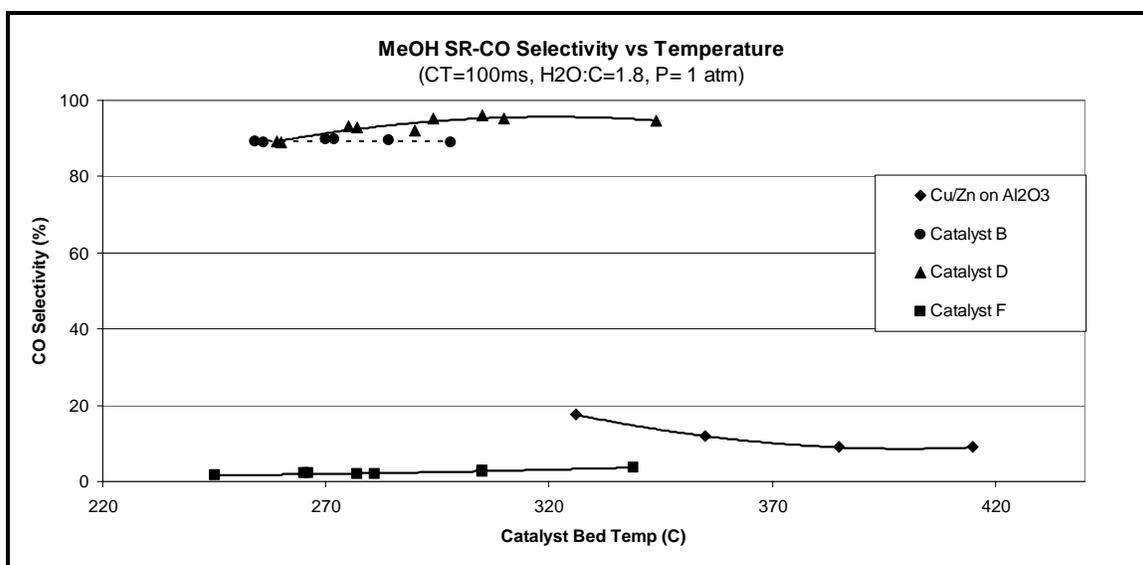
Figure 5. Methanol steam reforming catalyst CO selectivity results

Table 2. Typical reformate dry gas composition from catalyst F

Gas	Percentage
Hydrogen (H_2)	73.5%
Carbon Dioxide (CO_2)	25.8%
Carbon Monoxide (CO)	0.7%

3.2 Integrated fuel reformer system

The results reported in this section are for the integrated fuel processor system (Figure 6) composed of two vaporizers/preheaters, a reformer, a combustor, and a heat exchanger. The reformer has a volume of less than 5 mm^3 and a capacity of 200 mW$_t$. The combustor volume, also less than 5 mm^3, has a capacity of up to 3 W$_t$. The oversized combustor capacity allowed a wide range of operating conditions to be examined. The combustor fuel consisted of hydrogen or methanol. A thermocouple was inserted into the combustor to monitor the device temperature. The system was mounted inside a larger tube for testing (Figure 7).

The test stand (Figure 8) consisted of syringe pumps, gas controllers, vapor liquid separation units, and an online gas chromatograph. Syringe pumps fed the methanol/water mixture to the reformer at rates of 0.02 cc/hr to 0.1 cc/hr (20°C basis), and pure methanol to the combustor at rates of 0.1 cc/hr to 0.4 cc/hr (20°C basis). Air was fed to the combustor at rates between 8 and 20 sccm. The product reformate gases were fed, via a dri-rite tube to eliminate any residual water vapor, to an online micro gas chromatograph (Agilent QuadH).

The procedure for system start-up did not require electrical heating. Instead, hydrogen and air were fed to combustor to initiate combustion and heat the vaporizers. Once the vaporizers were heated to approximately 80°C, methanol was fed to the vaporizer. The hydrogen was slowly tapered off as the methanol feed was increased until only methanol and air were being fed to the combustor and the device was completely self-sustaining. The methanol air mixture was adjusted until the steam reformer reached the desired temperatures (250°C – 400°C), depending on the conditions being tested. The methanol/water solution feed to the steam reformer was then initiated.
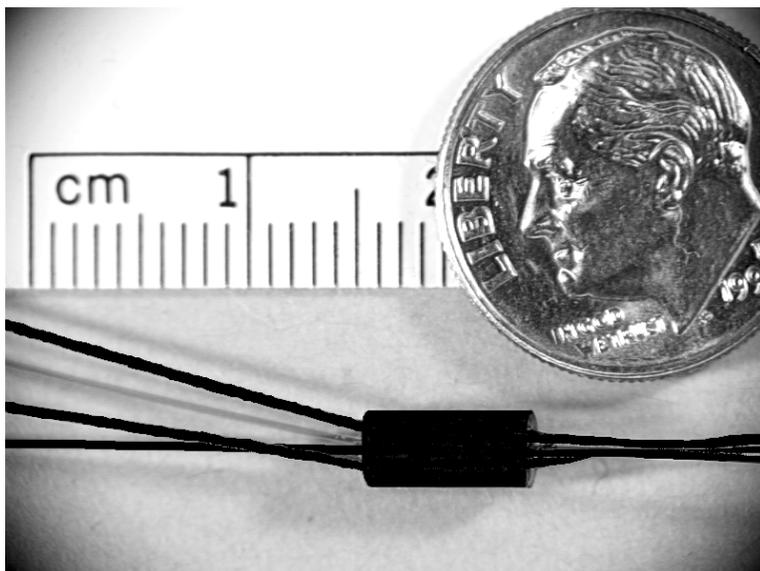

Figure 6. Integrated fuel processor system

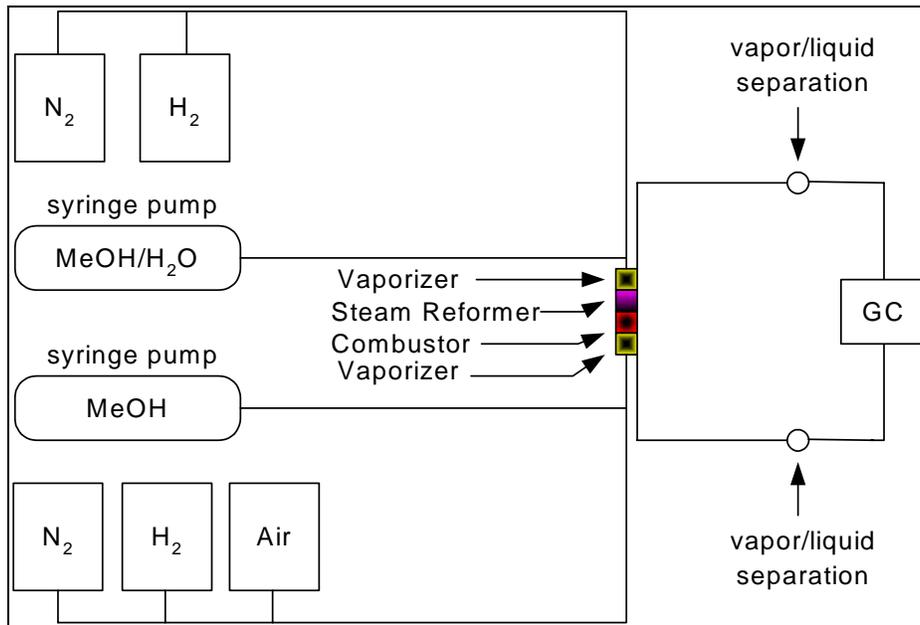Figure 7. Integrated reformer system mounted in the test stand

Figure 8. Test stand schematic

The reformer was operated over a wide range of conditions. In order to achieve 100% conversion, >400°C operating temperatures 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. Two hundred mW_t power was achieved with a thermal efficiency of 9%. The thermal efficiency was calculated by dividing the lower heating value of the hydrogen in the reformate stream by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor (see equation 1).

Efficiency = ΔH_chydrogen / (ΔH_cmethanol reformer feed + ΔH_c methanol combustor feed)   [1]

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

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 to 85% of the H_2 in a reformate stream for a net efficiency of ≈50%. Thus, it is anticipated that a fuel cell utilizing the reformate from this device could provide ≈100 mW_e, and the system (reformer + fuel cell) would have an efficiency of ≈9.6 % thermal and 4.8% net (with the fuel cell inefficiencies). As the reformer output was decreased, the efficiency also decreased. For example, when the reformer produced 70 mW_t (≈35 mW_e), the efficiency decreased to 6.4% (≈ 3.2% net). 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.

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 efficiency would be 4.94%. This small increase in efficiency (0.14%) is not sufficient to make such an integration appealing. Instead, an improved design would be more practical for increasing efficiency. From these results, improvements in the design of the system have been proposed and will be investigated. The tests also indicate it may be possible to build an efficient integrated system that can also reform higher hydrocarbons such as butane, which require higher processing temperatures.

4. SUMMARY AND CONCLUSIONS

A high-energy power supply for microelectronics is being developed at Battelle in conjunction with CWRU. The integrated fuel reformer system has been designed and built. A complete system would consist of liquid and gas delivery systems, valves, and packaging, and integration with a fuel cell.

Initial testing of the integrated fuel reformer system alone resulted in the production of 100 mW_e of hydrogen at a high efficiency of 4.8%, utilizing methanol as fuel. The reformate stream is composed primarily of hydrogen (>73%), with the rest consisting of approximately 26% carbon dioxide and 1% carbon monoxide. The low level of carbon monoxide is suitable for use with CWRU's fuel cell technology.

ACKNOWLEDGMENTS

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