Sub-watt Power Using an Integrated Fuel Processor and Fuel Cell

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Abstract

A sub-watt power system is being developed as an alternative to conventional battery technology to better meet energy and power densities needed for operating wireless electronic devices, such as microsensors and microelectromechanical systems. This system integrates a microscale fuel processor, which produces a hydrogen-rich stream from liquid fuels, such as methanol and butane, and a microscale fuel cell, which uses the hydrogen as fuel to produce electric power. Battelle, Pacific Northwest Division and Case Western Reserve University are developing and demonstrating this technology for the Defense Advanced Research Projects Agency. This paper describes work being performed by Battelle on the fuel processor, in particular, catalyst and reactor design and testing.

The microscale fuel processor (integrated vaporizer/steam reformer/combustor) assembled, fabricated, and tested during this study generated an equivalent power level of 10 to 500 mW_e. This steam reformer test system has a reactor volume of less than 5 mm^3. Catalyst testing achieved a near-maximum theoretical conversion for methanol with <1% CO in product H_2 gas. High conversion and H_2 selectivity was also achieved during catalyst testing with butane, but at higher temperatures.

Introduction

The availability of onboard power, coupled with wireless data transmission, will open numerous possibilities for autonomous devices for remote or difficult-to-access locations. Current battery systems have two problems: excessive weight/bulk, and reduced mission duration. Compact fuel cell systems operating on liquid hydrocarbon fuels offer an efficient, light-weight alternative to batteries, allowing for greater portability and longer mission lifetime. For instance, the energy densities of diesel fuel and methanol are each at least an order of magnitude greater than that of lithium-ion batteries. A hydrocarbon-based fuel

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cell system operating at just 5% overall efficiency has a higher energy density than a lithium polymer battery

Under a program for the Defense Advanced Research Projects Agency, Battelle, Pacific Northwest Division (Battelle) and Case Western Reserve University (CWRU) are developing and demonstrating an integrated fuel cell and fuel processor for microscale (50- to 500-mW_e) power generation. This alternative power source has many potential advantages over conventional batteries for operating wireless electronic devices (e.g., microsensors and microelectromechanical systems), especially in terms of energy and power densities.

The technology consists of a microscale reformer for hydrocarbon fuels, based on a concept developed at Battelle, coupled to an elevated-temperature (150°C to 200°C) proton exchange membrane (PEM) fuel cell developed by CWRU. This paper describes the work being performed by Battelle on the fuel processor, in particular, catalyst and reactor design and testing.

The overall power system will eventually include several subsystems: fuel storage, fuel processor, synthesis gas treatment (optional), and fuel cell, along with associated peripherals such as pumps and control valves. The fuel processor contains a reforming reactor, combustion reactor, and heat exchangers. The fuel from storage is mixed with air and water in a fuel processor system that operates at 600°C to 700°C for butane and 250°C to 550°C for methanol. Heat generated in the combustion reactor is transferred to the endothermic reforming reactor to produce the H_2-containing synthesis gas. The synthesis gas may be processed directly in the fuel cell or treated to minimize the CO concentration, depending on the type of fuel cell. The fuel cell converts H_2 and O_2 (from air) to electrical power and water.

Experimental Results and Discussion

The testing described below was performed in different apparatuses. The catalyst testing was performed in dedicated catalyst test equipment while the micro-reactors were tested in a separate dedicated system. Since the catalyst performance and requirements are critical to final reactor design, the catalyst testing must be done first.

Reformer Catalyst Testing Results - Butane

A novel catalyst was used to examine reforming butane to hydrogen and carbon monoxide at 10 to 35 ms contact times in the temperature range of 500°C to 900°C. Figure 1 shows butane conversion (top) and hydrogen and methane selectivity (bottom) as a function of temperature and contact time. The data in

Figure 1 show that 100% butane conversion is achieved at approximately 600°C and at contact times of 25 and 35 mS. For a contact time of 10 mS, 100% butane conversion is not achieved until an operating temperature of over 750°C is reached. Longer contact times and higher operating temperatures also favor hydrogen selectivity. However, only at the highest temperatures does this selectivity approach that predicted by equilibrium.

The data show that approximately 10.5 moles of hydrogen can be produced per mole of butane reacted at the higher temperatures and longer contact times. In addition, at the longer contact times and higher temperatures, the hydrogen yield approaches the yield predicted at equilibrium. The catalyst volume of the reformer reactor operating at 100 ms contact time is still less than 5 mm^3.
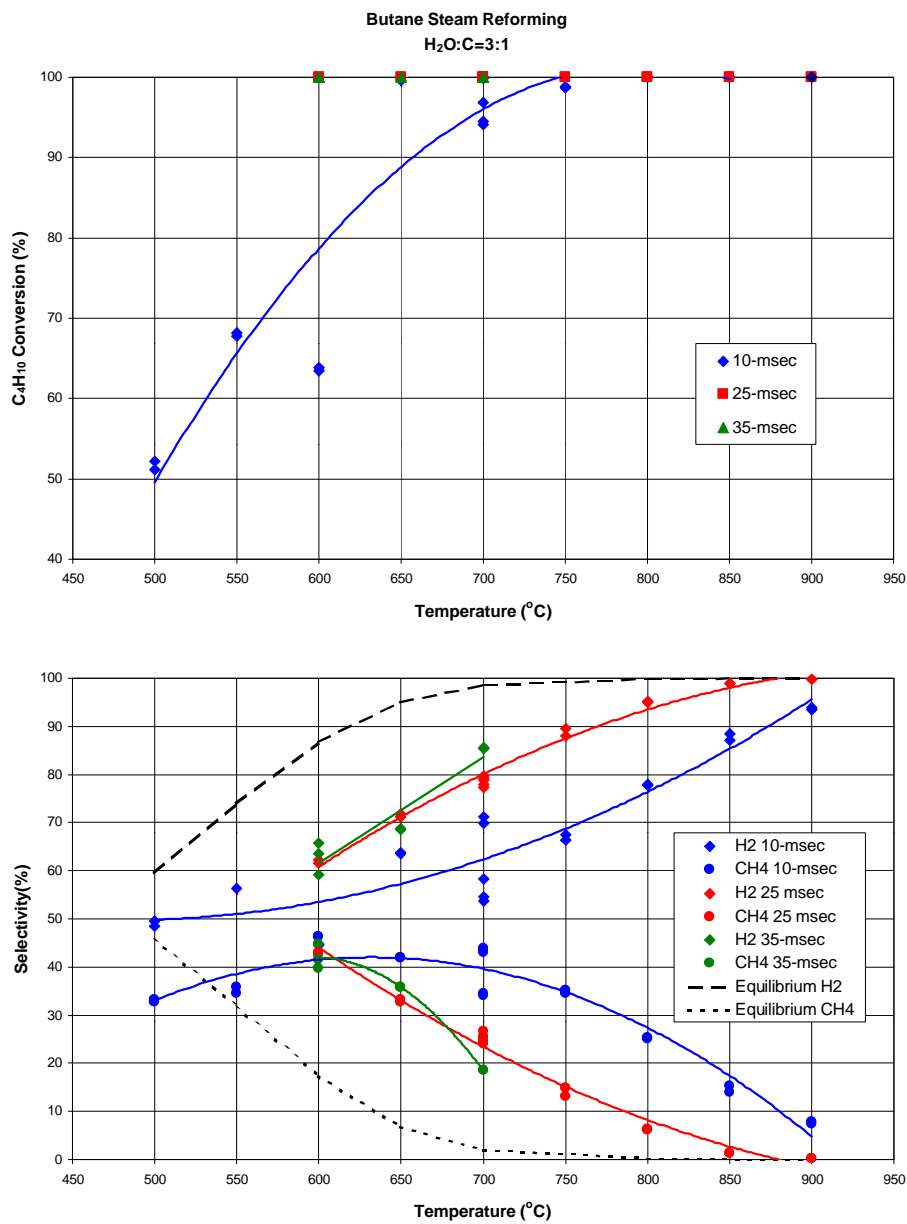
Figure 1. Butane Steam Reforming Catalyst Testing (3:1 Water: Carbon Molar Ratio). Butane conversion (top); selectivity (bottom).

Reformer Catalyst Testing Results - Methanol

Three types of catalysts were tested, labeled A, B, and C. Catalysts B and C were tested initially and performed well, but lower operating temperatures and lower carbon monoxide selectivity was desired. Consequently, a novel catalyst (labeled A) was tested at 300 msec contact times in the temperature range of 240°C to 400°C.

All testing reported here was conducted using a water:methanol molar ratio of approximately 1.8:1 in the incoming feed. Figure 2 shows methanol yield (left axis) and carbon monoxide yield (right axis) as a function of temperature. All three different catalysts were evaluated at these conditions. The data show the dramatic improvement in both methanol conversion and carbon monoxide content in the off-gas when going from catalyst C to catalyst A. For catalyst C, a methanol conversion of less than 80% was achieved at nearly 400°C, while nearly 100% methanol conversion was achieved at 360°C using catalyst B, and nearly 90% methanol conversion was achieved at temperatures as low as 280°C using catalyst A. For both catalyst B and catalyst C, the carbon monoxide concentrations in the off-gas were high, ranging from approximately 10 mol% to over 27 mol%. For catalyst A, on the other hand, the off-gas carbon monoxide concentrations were extremely low, less than 0.5 mol% for all of the conditions tested.

The hydrogen yield is shown in Figure 3 for these same catalysts. The data show that catalyst A is superior to the other two catalysts from this perspective as well. Hydrogen yields of nearly 3 moles hydrogen per mole methanol converted are achieved for catalyst A. This is very close to the theoretical yield based on the reaction given below:

$$CH_3OH + H_2O \longrightarrow CO_2 + 3H_2$$
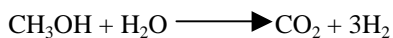
The data are plotted in terms of equivalent electrical energy produced per methanol converted ("energy density") in Figure 4. In this figure, a fuel cell efficiency of 64% is assumed. The solid line shown in Figure 5 is the theoretical "energy density" assuming reaction (1) and a fuel cell efficiency of 64%. As can be seen, the performance of catalyst A comes very close to the theoretical "energy density."

This testing showed that at an operating temperature of approximately 280°C, catalyst A can convert over 90% methanol to yield nearly 3 moles of hydrogen/mole methanol converted. The concentration of carbon monoxide in the off-gas is less than 0.5 mol%. Testing is continuing develop catalyst with a lower operating temperature.
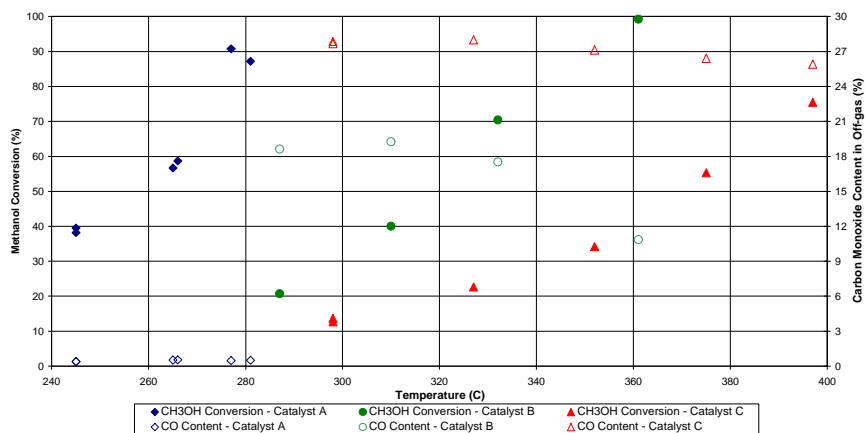
Figure 2. Methanol Conversion and Carbon Monoxide Content. Steam reforming test conditions: 1.8:1 water:methanol (mol:mol) feed, 300 msec contact time, three different catalysts.
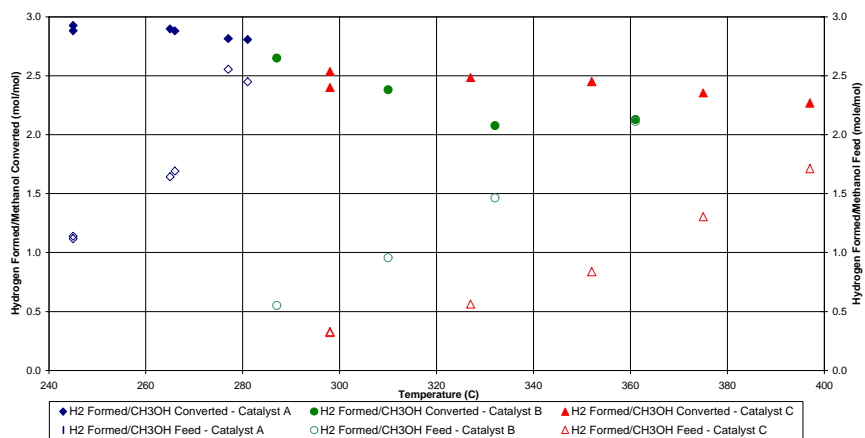

Figure 3. Hydrogen yield. Steam reforming test conditions: 1.8:1 water:methanol (mol:mol) feed, 300 msec contact time, three different catalysts.
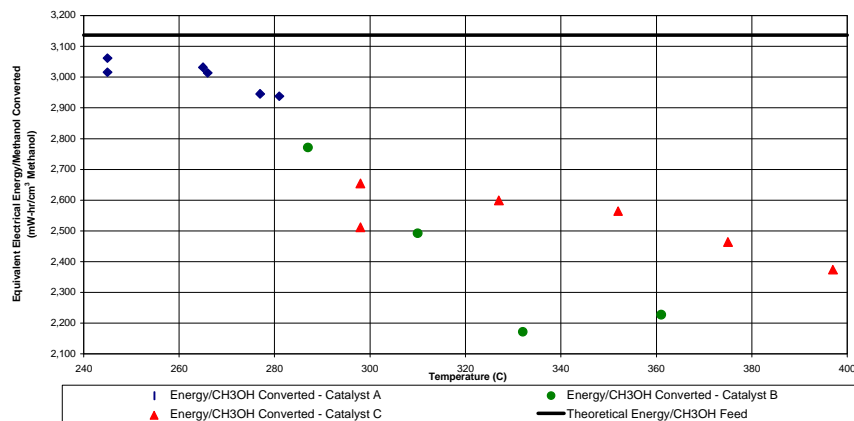
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Figure 4. Equivalent Electrical Energy Production (64% fuel cell efficiency, methanol density = 0.79 g/ml assumed). Steam reforming test conditions: 1.8:1 water:methanol (mol:mol) feed, 300 msec contact time, three different catalysts.

Assembly and Fabrication of Steam Reformer/Combustion Test System

The 50- to 500-mW_e integrated vaporizer/steam reformer/combustor test system is illustrated in Figures 5 and 6. Syringe pumps are used to supply the methanol/water mix (1.8:1 water:carbon molar ratio) to the steam reformer and pure methanol to the combustor. The methanol/water flow rates range from approximately 0.03 to 0.1 ml/hr (20°C basis). The mixed water and fuel then enter a vaporizer section in the integrated device and pass through the catalyst bed through a vapor/liquid separator section and exit to an online gas chromatograph for analyses. The steam reformer catalyst reactor volume is less than 5 mm^3.

Before the methanol was fed to the combustor, hydrogen (in the presence of air) was used as the fuel source to initiate the combustion. The hydrogen was fed to the reactor via a mass controller. The air was fed at flow rates ranging from approximately 8 to 14 sccm; the hydrogen was fed at rates from 1 to 5 sccm, and the methanol was fed at rates from approximately 0.05 to 0.2 ml/hr (20°C basis).

The experimental fuel processor below contains two reactors and a heat exchanger. The reformer has a volume of less than 5 mm^3 with a capacity of 200 mW. The combustor volume has a volume less than 1 mm^3 and a capacity of 3 W. The combustor capacity is larger than necessary so that a full range of conditions can be studied.
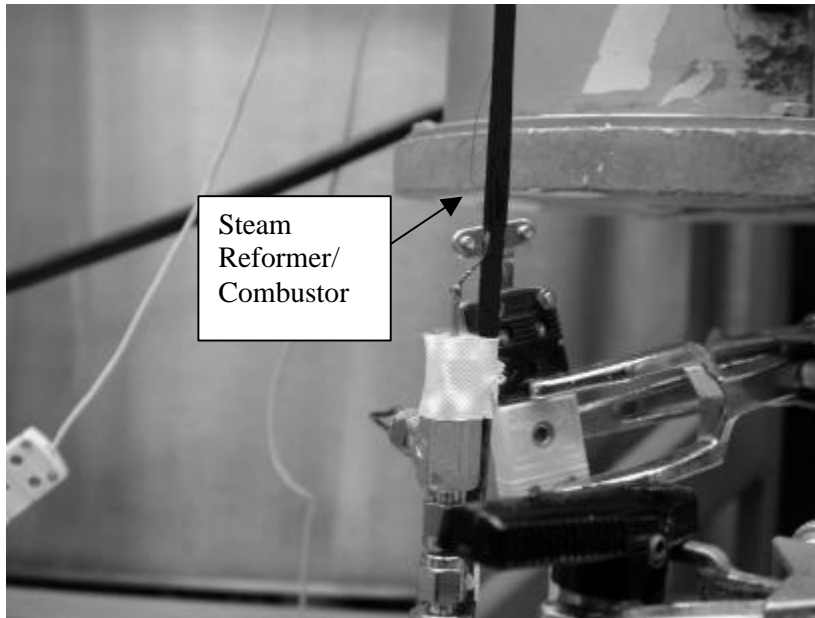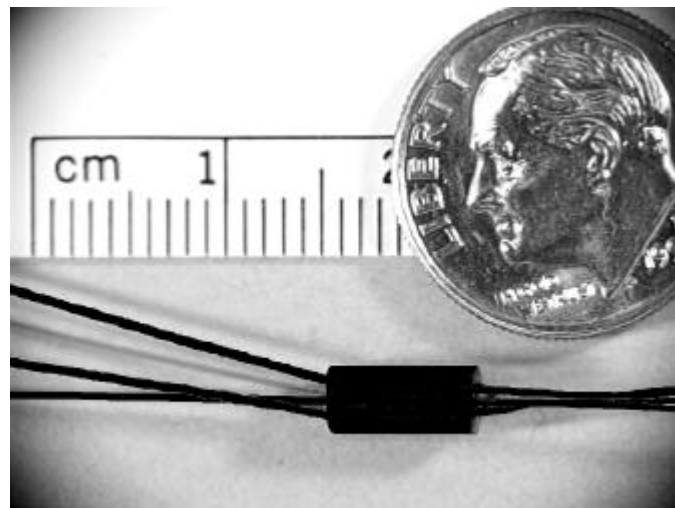
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Figure 6.　　　　Above - Integrated Vaporizer/Steam Reformer/Combustor Test System (50- to 500 mW$_e$). The integrated reactor is mounted in a tube.
　　　　　　　　Below - Experimental Fuel Processor

Summary and Conclusions

Catalyst test data from butane reforming show that 100% conversion is achieved at approximately 600°C and contact times of 25 and 35 mS. For a contact time of 10 mS, 100% butane conversion is not achieved until an operating temperature of over 750°C is reached. Longer contact times and higher operating temperatures also favor hydrogen selectivity. However, only at the highest temperatures does this selectivity approach that predicted by equilibrium. The catalyst volume of the reformer reactor operating at 100 ms contact time is 1 to 5 mm^3. Hydrogen yield data show that approximately 10.5 moles of hydrogen can be produced per mole of butane reacted at the higher temperatures and longer contact times.

Catalyst data from methanol reforming show that 100% conversion is possible with high H_2 selectivity and low CO concentration.

A 10- to 500-mW$_e$ steam reformer test system has been fabricated and assembled with a reactor volume of less than 5 mm^3. Shakedown and preliminary testing of the steam reformer reactor has been completed.