IECEC 2002 Paper No. 20074

Micro-fuel Processors for a 15-25 Watt Fuel Cell Battery Hybrid Power Supply

Jamie Holladay
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-373-1473, 509-376-5106, JD.Holladay@pnl.gov

John Hu
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-376-0427, 509-376-5106, Jianli.Hu@pnl.gov

Daniel Palo
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-376-4181, 509-376-5106, Daniel.Palo@pnl.gov

Ya-Hui Chin
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-376-0134, 509-376-5106, Ya-Hui.Chin@pnl.gov

Ed Baker
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-375-6720, 509-372-4732, Eddie.Baker@pnl.gov

Robert Dagle
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-376-5354, 509-376-5106, Robert.Dagle@pnl.gov

ABSTRACT

A 15 W_e portable hybrid power supply composed of a PEM fuel cell and a methanol fuel processor is being developed for the U. S. Army. This paper reports on fuel processor sub-system development progress. The methanol steam reformer system is composed of vaporizers/preheaters, a catalytic combustor, a methanol steam reformer, and heat recuperators. These unit operations have been thermally integrated into a single fuel processing device. The fuel processor was evaluated over a wide range of conditions up to 52 W_t.

The device efficiency was estimated to be 60% for the fuel processor, and 29% for the system with a hypothetical fuel cell. The corresponding energy density was estimated at 850 Whr/kg and 985 Whr/L, assuming continuous operation over a 14 day mission while supplying a nominal 15 W_e of power. This energy density is several times that of currently available lithium-ion batteries.

The final system will consist of the fuel cell, fuel processor, and a secondary battery. The fuel cell coupled with the reformer will provide the primary source of power. The battery will provide start-up power and load leveling capabilities.

INTRODUCTION

Twenty-first century portable electronic technology such as PDA's, cellular phones, notebook computers, and MEMS have fueled a need for new high-energy, small volume power supplies for both military and commercial markets. Wireless devices are currently limited to twentieth century battery technology, which by itself is insufficient to provide the mandatory long term power these new microelectronic systems require. Hybrid systems composed of a microscale fuel reformer, proton exchange membrane (PEM) fuel cells, and secondary batteries would combine the high energy of liquid hydrocarbon fuels with clean fuel cell power, and the convenience of batteries. Battelle, Northwest Division (Battelle), is taking the lead in the development of hydrocarbon-fueled portable power supplies to meet this need.

Conversion of the energy stored in hydrocarbon fuels in a compact and efficient system is a complicated challenge. The energy stored in hydrocarbons ranges from 5.6 kWhr/kg for methanol to over 12 kWhr/kg for higher hydrocarbons such as butane, iso-octane (gasoline), or diesel. Traditionally this chemical energy has been converted to electrical energy by means of combusting the hydrocarbon to generate high quality steam to turn turbines. A potentially more efficient and elegant process is to reform the hydrocarbon and feed the resulting hydrogen-rich gas to a fuel cell, which reacts the hydrogen with oxygen (from air) to produce electricity, some heat, and clean water. Companies such as H-Power (Elkaim, 2000), Englehard (Ruettinger et al., 2002), United Technologies Corp. (Pietrogrande and Bezzeccheri, 1993) and others have demonstrated the feasibility of this approach on a large scale for stationary applications.

Under contract with the U.S. Army (CECOM), Battelle, is currently developing a hybrid power system designed to provide 15 watts nominal and 25 watts peak of electric power for the dismounted soldier. The system is being designed for continuous use over a 14 day mission. The final system will include an integrated micro-technology-based fuel

processor, a PEM fuel cell, and a secondary battery. Initial development is focused on methanol as the fuel due to its ease of reforming (Palo et al., 2002), with systems using higher hydrocarbons to be developed later. The technology being reported in this paper is suitable for both military and commercial use.

FUEL PROCESSING

Often fuel processors for PEM fuel cells are composed of five main unit operations:

1. fuel vaporizers/preheaters,
2. fuel reformer,
3. gas clean-up unit(s) to remove excess carbon monoxide, a PEM fuel cell poison,
4. heat exchangers (recuperators), and
5. a combustor.

The balance of plant devices, including pumps, blowers, valves, insulation, and controls, ensure the system operates properly. Battelle has been in the forefront of micro chemical process development which allows significant size miniaturization, often by an order of magnitude or more, for the unit operations required for fuel processing (Brooks et al., 1998; Zilka-Marco et al., 2000; VanderWiel et al., 2000; Wegeng et al., 2001; Palo et al., 2002; Holladay et al., 2002).

Fuel reforming is typically accomplished by steam reforming, partial oxidation, or autothermal reforming. Each technique has advantages and disadvantages associated with it (Pietrogrande and Bezzeccheri, 1993). A general fuel processing equation is:

$$C_aH_bO_c + x(O_2+3.76N_2) + (y+2x-2z-c)H_2O = yCO + zCO_2 + (a-y-z)CH_4 + 3.76xN_2 + (b/2-2a-c+3y+4z-2x)H_2$$

This general fuel processing equation can be simplified by identifying the reforming technique and the fuel. Due to the potential high efficiency of steam reforming, it was chosen for this work.

Battelle has been aggressively developing catalysts for various applications, including micro-process technology. One area of significant focus has been steam reforming for multiple hydrocarbon fuels. Steam reforming of methanol, propane, butane, iso-octane, synthetic diesel, and de-sulfurized JP-8 has been demonstrated at low contact times[1] of 10-200 ms or high gas hourly space velocities of 10^4-10^5 hr^{-1}. This significant improvement in catalyst technology allows drastic reduction in the catalyst bed size required for steam reforming at a given temperature and flow rate (Palo et al., 2002, Holladay et al., 2002). Since methanol steam reforming is the subject of this work, the general equation can be simplified to:

$$CH_3OH + (y-2z-1)H_2O = yCO + zCO_2 + (1-y-z)CH_4 + (3y+4z-1)H_2.$$

[1] Contact time is the inverse of gas hour space velocity and is based upon the entire volume of the reactor.

EXPERIMENTAL

The ultimate goal is a complete system containing all the unit operations thermally integrated, along with the balance of plant, battery, and fuel cell. The early stages of development include the design, fabrication, and testing of individual unit operations, followed by their thermal integration, leading to a complete system demonstration. The testing of the individual unit operations (vaporizers, combustors, etc.) has been reported previously (Palo et al., 2002). This paper will discuss the thermal integration of these unit operations. Figure 1 contains the process flow of the system and a picture of the system reported by Palo et al. (2002).

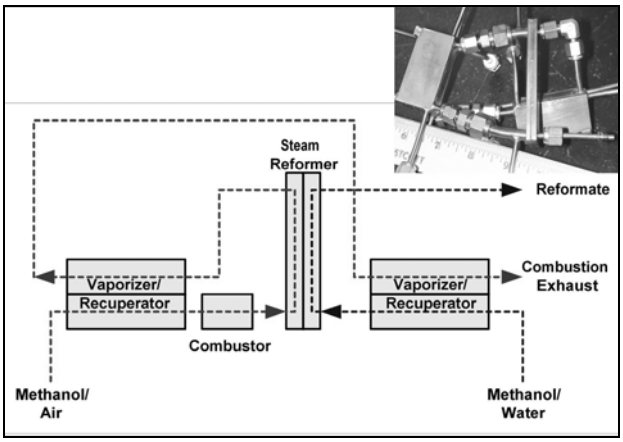

FIGURE 1. FLOW SCHEMATIC OF PROCESS AND PICTURE OF PREVIOUSLY REPORTED SYSTEM TEST.

Battelle's extensive facilities allowed catalyst preparation, device fabrication, system testing, and product analysis to be performed on site. The system was composed of stainless steel units. Strategically placed thermocouples and pressure transducers allowed online data acquisition.

The system was heated by catalytic combustion of methanol to provide the energy for liquid vaporization and preheat, as well as the heat of reaction for the endothermic methanol steam reforming reaction (+ 50 kJ/mol). Methanol for combustion was fed via a HPLC pump and compressed air was used to provide the oxygen.

A mixture of methanol and water (1:1 ratio by weight) was fed to the system by another HPLC pump. Vaporization, preheating, and steam reforming were accomplished in the thermally integrated unit. The product stream (reformate) was chilled, passed through a vapor-liquid separator and fed to an online gas chromatograph (Agilent Tech. Micro-GC) for analysis. The detection limit for the GC was approximately 100 ppm.

RESULTS AND DISCUSION

Six unit operations were successfully integrated into a single reactor system. The operations included two vaporizers/preheaters, a catalytic combustor, a steam reforming reactor, and two recuperators. The system had a volume of less than 25 cm^3 and a weight of less than 100 g excluding inlet and exit tubing. The unit has eight inlet and outlet ports. Four of the ports allow for the combustor and reformer reactants to enter and products to exit the system. The other four ports allow for thermocouple and pressure transducer access to the inside of the system. The device is pictured in Figure 2.

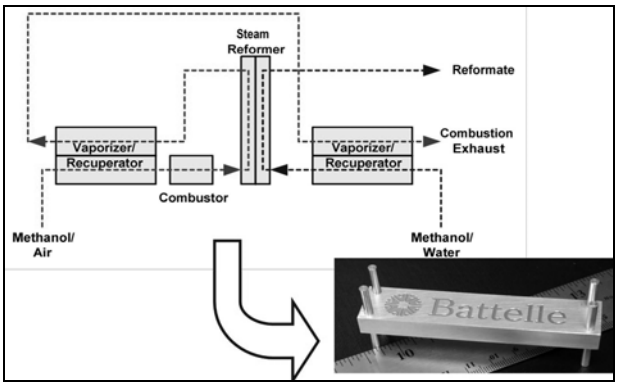

FIGURE 2. THERMAL INTEGRATION OF PROCESSOR UNIT

The catalytic combustor was electrically preheated at startup in order to initiate methanol combustion. Once methanol combustion was achieved, the electric heater was turned off. In a practical device, small electric heaters powered by the secondary batteries could provide the initial heating if alternative startup methods are not developed. Startup could be accomplished in under ten minutes, and alternative (faster) methods are under development.

The processor was operated over a range of conditions to obtain performance data. The hydrogen quantities produced were sufficient to provide between 10 W_t and 52 W_t of power, based on hydrogen's lower heating value. Table 1 specifies typical operating conditions for the device. Under these conditions methanol conversion was >99%, and the typical dry gas reformate composition was 73-74% hydrogen, 25-26% carbon dioxide, and 0.4-0.7% carbon monoxide. Any methane produced was undetectable.

A PEM fuel cell cannot tolerate above approximately 100ppm carbon monoxide under normal operating conditions. Typically a water-gas-shift (WGS) reactor followed by a preferential oxidation (PrOx) reactor is used to clean the reformate stream to this low CO condition (Pietrogrande and Bezzeccheri, 1993). The WGS reactor is used to reduce the carbon monoxide level to below 1-2%, and the PrOx reactor is used to further reduce the CO to levels appropriate for PEM fuel cells. Since the reformate exiting our system contains less than one percent carbon monoxide, no WGS reactor is necessary. This eliminates a unit operation from the final system, thus simplifying it greatly. Further reformate conditioning needs to be accomplished to reduce the carbon monoxide to appropriate levels. Investigations into carbon monoxide cleanup are underway, but will not be discussed in this paper.

TABLE 1. DEMONSTRATION OPERATING CONDITIONS AND RESULTS

Operating Conditions	
Reformer Temperature	320°C
Pressure	1-2 psig
Contact Time	150 ms
Water/methanol molar ratio	1.8
Fuel Processor Results	
Methanol conversion	>99%
Gas Composition	
Hydrogen	73.3%
Carbon Dioxide	26.3%
Carbon Monoxide	0.42%
Hydrogen production rate	29 W_t
Methanol feed rate	48.3 W_t
Fuel processor thermal efficiency	60%
Fuel Cell Power Estimate- assume fuel cell 60% efficient with 80% hydrogen utilization	14 W_e
Fuel Processor/Fuel Cell System Efficiency	29%
Estimated System Energy Density- assuming fuel processor + fuel cell =1kg and 14 day mission	850 Whr/kg
	985 Whr/L

Fuel cell power estimates, efficiencies, and energy densities can be approximated with a few reasonable assumptions. Fuel cell power was calculated assuming either no further reformate conditioning was necessary or that only negligible amounts of hydrogen would be lost during a CO cleanup stage. In the final system, the reformate would be fed to a PEM fuel cell with an expected efficiency of 60%, and a hydrogen utilization of 80%, or a net efficiency of 48%. In other words, 48% of the thermal power in the hydrogen feed would be converted to electrical wattage in the fuel cell.

Thermal efficiency was calculated as the lower heating value of the product hydrogen divided by the lower heating value of the methanol fed to the system:

$$\eta_t = \frac{LHV_{hydrogen}}{LHV_{combustion\_meoh} + LHV_{reforming\_meoh}}$$

where LHV is the lower heating value.

This equation assumes hydrogen not reacted by the fuel cell is not recycled into the system, that an insignificant amount of hydrogen will be consumed

during CO cleanup, or a fuel cell which can tolerate this level of carbon monoxide is available.

Electrical efficiency (fuel processor + fuel cell) is calculated by dividing the assumed fuel cell power by the lower heating value of the methanol fed to the system:.

$$\eta_e = \frac{W_e}{LHV_{combustion\_meoh} + LHV_{refor\min g\_meoh}}$$

where LHV is the lower heating value and W_e is the estimated fuel cell power out.

This equation is subject to the same assumptions as the previous equation. The system thermal efficiency was 60% and the electrical efficiency was 29% over the range that was tested. Improvements in insulation and removal of the thermocouple ports are expected to improve the efficiency to even higher levels.

Gravimetric and volumetric energy densities were determined assuming that the final fuel cell/fuel processor system will weigh 1 kg (excluding the fuel and water). From our systems studies, it is believed that this target can be achieved with little development in current state-of-the-art pumps, fans, etc. It was also assumed that the system would operate for 14 days continuously, the methanol water mixture being a 1:1 ratio by weight, and that all necessary water would be carried. Obviously, higher energy densities could be achieved by recycling the water in the system; therefore, the numbers presented represent a ”worst case” scenario. The energy density using these assumptions was calculated to be 850 Whr/kg and 985 Whr/L. Table 2 compares the fuel processor/fuel cell system with batteries that are being evaluated for use in the Army. As seen in the table, the fuel processor/fuel cell system weighs 1/10 to 1/3 that of corresponding batteries, and are 1/11 to 1/3.5 the volume for 15 to 25 W_e continuous power for 14 days.

Figure 3 contains an artist’s rendition of a packaged power system that includes the fuel cell, fuel reformer, secondary battery, balance of plant components, and two removable fuel containers that the soldier can refill as needed.

TABLE 2. BATTERY COMPARISON TABLE

Model	Chemistry	Whr/kg	Whr/L	P/S$^{\phi}$
BB-2590U	Li-ion	84	109	S
L17	Li-ion	118	180	S
LI 1.5	Li-ion	136	128	S
LM11	$LiMnO_2$	196	265	P
BA-x847A/U	$LiMnO_2$	226	87	P
LMP 13.5	$LiMnO_2$	308	107	P
Fuel Processor*	MeOH reforming	850	985	n/a

(Adapted from Feldman 1999)

$^{\phi}$P= primary battery chemistry; S= secondary battery chemistry

* Assuming 14 day continuous use at 23 W_e output.

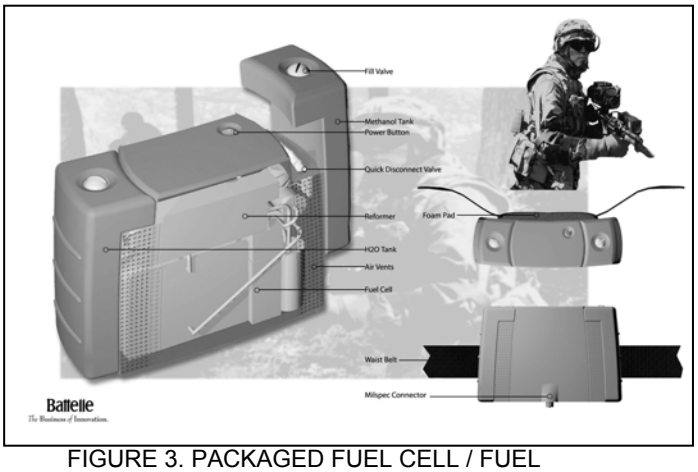

FIGURE 3. PACKAGED FUEL CELL / FUEL PROCESSOR / BATTERY HYBRID POWER SUPPLY FOR THE DISMOUNTED SOLDIER

CONCLUSION AND FUTURE WORK

Thermal integration of a fuel processor has been completed. The processor consists of multiple vaporizers/preheaters and heat recuperators, coupled with a catalytic combustor, and a methanol steam reformer. The device has been demonstrated over a range of conditions up to 52 W_t.

The fuel processor efficiency and energy density have been estimated by assuming a final hardware mass of 1 kg and a 14-day mission life. The thermal efficiency was determined to be 60% and the estimated overall efficiency, with assumptions of how well the fuel cell will perform, was 29%. This translates into energy densities of 850 Whr/kg and 985 Whr/L. These energy densities are several times that of currently available lithium-ion batteries.

Initial systems studies indicate that it is feasible to couple this unit with a fuel cell and a secondary battery to make a packaged hybrid power supply for use in portable power applications.

Continued fuel processor development is expected to significantly increase the efficiency and energy density of the system. Carbon monoxide removal technology is also being developed and will be integrated into the system in the near future. A bread board of the fuel cell and fuel processor with appropriately sized balance of plant components is also under development.

ACKNOWLEDGMENT

This work was funded by the U.S. Army Communications-Electronics Command, and their support is gratefully acknowledged.

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