Development of a soldier-portable fuel cell power system
Part I: A bread-board methanol fuel processor

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Abstract

A 15-W_e portable power system is being developed for the US Army that consists of a hydrogen-generating fuel reformer coupled to a proton-exchange membrane fuel cell. In the first phase of this project, a methanol steam reformer system was developed and demonstrated. The reformer system included a combustor, two vaporizers, and a steam reforming reactor. The device was demonstrated as a thermally independent unit over the range of 14–80 W_t output. Assuming a 14-day mission life and an ultimate 1-kg fuel processor/fuel cell assembly, a base case was chosen to illustrate the expected system performance. Operating at 13 W_e, the system yielded a fuel processor efficiency of 45% (LHV of H_2 out/LHV of fuel in) and an estimated net efficiency of 22% (assuming a fuel cell efficiency of 48%). The resulting energy density of 720 Wh/kg is several times the energy density of the best lithium-ion batteries. Some immediate areas of improvement in thermal management also have been identified, and an integrated fuel processor is under development. The final system will be a hybrid, containing a fuel reformer, a fuel cell, and a rechargeable battery. The battery will provide power for start-up and added capacity for times of peak power demand. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The remarkable recent advances in wireless and portable communications devices (e.g. laptop computers, cellular phones, portable digital assistants) have fueled a need for high-energy-density portable power sources for consumer use. In a similar way, interest in portable power sources has increased in the military and intelligence communities, where portable electronics are seeing increased use and are currently dependent on batteries to supply electrical power for long-duration missions.

The low energy densities of current battery systems contribute to the excessive weight and bulk of portable equipment, and severely limit the duration of military operations using portable electronic devices. As a result, several options for higher-energy-density power supplies have been put forth, as seen in Table 1. While much progress has been made in battery technology, this power source tends have limited energy density—currently at 150 Wh/kg, and projected to reach 300 Wh/kg with future advances.

One alternative source is a fuel cell operating on stored hydrogen, which currently offers energy densities ranging from 500 to 1000 Wh/kg. A second alternative, with a much higher energy density, is a fuel cell system fueled by a liquid hydrocarbon. As shown in Table 1, both methanol and *n*-dodecane (diesel fuel) offer much higher energy densities than either batteries or stored hydrogen, making them both attractive sources for portable power. Clearly, a hydrocarbon-fueled fuel cell would be the preferred energy source for a portable power system if a rugged, reliable, and lightweight fuel processor were available to efficiently convert hydrocarbons to hydrogen. An appropriate fuel processor would produce hydrogen of sufficient quantity and purity to drive a proton-exchange membrane (PEM) fuel cell, and would do so within a small volume. Such a system is the focus of this paper.

The search for a compact, efficient fuel processing device leads naturally to micro-process technology. Micro-process technology involves minimizing the characteristic internal dimensions of reactors and heat exchangers. Such devices, having channel widths on the order of hundreds of microns (microchannels), exhibit dramatically reduced heat- and mass-transfer resistances relative to conventional unit operations. Reducing such resistances allows chemical reactions

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Table 1
Comparison of energy densities of various power sources

Fuel	LHV (kJ/mol)	Energy density (kWh/kg)	Efficiency required (to match Li-ion batteries)
Methanol	639	5.6	5.5%
n-Octane	5100	12.3	2.4%
n-Dodecane	7552	12.3	2.4%
H_2 storage	242	0.5–1.0	30–60%
Lithium polymer battery	–	0.3 (projected)	

to proceed at much higher rates—much closer to the intrinsic kinetics.

For several years, Battelle has led the development of micro-process technology for various applications and device sizes. These technologies include fuel vaporization [1–4], gas conversion [5–7], fuel processing [1,6–12], heat transfer [2–4,13,14], mass transfer [15,16], catalytic combustion [3,4,13,17], and partial oxidation [12]. In each application, the microchannel architecture drastically reduces the heat- and mass-transfer resistances relative to conventional systems, providing for increased efficiency.

Many of these advances were built upon Battelle's aggressive effort to develop catalysts for micro-process applications. One major focus has been on steam reforming catalysts for various hydrocarbon fuels. Steam reforming of methanol, propane, butane, *iso*-octane, desulfurized diesel, and desulfurized JP-8 has been demonstrated at millisecond contact times[1] (GHSV: 10^4 to 10^5 h^{-1}). This represents a drastic reduction in the size of the catalyst bed necessary to effect steam reforming at a given temperature.

Such micro-process and catalyst technology is a natural fit for portable power systems, where size and weight must be minimized. For instance, the required catalyst bed volume for a 15-W_e steam reformer operating at 100 ms contact time is less than 0.5 cm^3. When compared to traditional reforming technology with contact times on the order of seconds, this translates to a correspondingly small device size. As a result, the majority of the weight and bulk of the final system will be dictated by the related fuel supply rather than the fuel processor (based on multi-day missions).

Under the research project discussed here, funded by the U.S. Army Communications-Electronics Command, Battelle is developing a 15-W_e fuel processing system suitable for portable power applications. This portable fuel processor is expected to provide a clean hydrogen stream to a small PEM fuel cell according to the target specifications listed in Table 2. The "bread-board"[2] device represents the first step of this project—demonstration of combustion,

steam reforming, and vaporization at the 15-W scale in a compact, though not fully integrated system.

2. Objectives

The Army's desire for improved portable power sources arises from a broader plan to decrease the weight and bulk of the its combat divisions, thus increasing mobility and effectiveness. In terms of energy density, the Army has certain milestones, based on projected power needs for the future soldier. These milestones are listed in Table 3. While the future combat power system will likely operate on diesel or some other logistics fuel, commercial use and the first military applications are focused on methanol. The lower reforming temperatures of methanol allow for reduced heat losses, require less insulation, and simplify the thermal management of the integrated system. A comparison of Tables 1 and 3 reveals that power systems operating on methanol are capable of reaching at least the first two energy density targets set by the Army.

Beyond 2005 or 2008, higher-energy-density fuels such as diesel must be employed if the Army's energy density goals are to be reached. This also points out the inability of current hydrogen storage and battery technology to meet the Army's out-year goals.

A diesel-fueled system will require higher reforming temperatures and the addition of more extensive gas cleanup

Table 2
Target specifications for soldier-portable power system

Average power	15 W_e
Peak power	25 W_e
Volume	<100 cm^3
Weight (excluding fuel)	<1 kg

Table 3
Energy density goals for power sources for US Army [18]

Year	Required energy density (Wh/kg)
2003	270
2005	1450
2008	3100
2018–25	5900

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[1] Contact time is the inverse of gas hourly space velocity (GHSV) and is based on the entire volume of the reactor.

[2] The term "bread-board" refers to a process train in which all major components are present and connected, but not fully integrated.

steps, such as water-gas shift. This results in a more complicated fuel processor, both thermally and chemically, which will require a greater development effort than is required for a methanol-fueled system. The development of a diesel-fueled portable power system is currently ongoing, but beyond the scope of this paper.

3. Experimental

While the ultimate goal of the fuel processor development is a fully integrated unit containing all necessary unit operations, the early stages of development include the design, fabrication, and testing of individual unit operations. This allows for the working out of problems separately for individual components in the system. As separate unit operations are tested and improved, they are integrated into the bread-board system where they can be demonstrated in conjunction with each other. This demonstration will be followed by the full integration of all unit operations into a single rugged device suitable for field testing, then by complete system integration including the fuel cell and peripherals. Combustor and steam reformer catalyst testing and improvement are conducted simultaneously with the hardware development.

All catalyst preparation, device fabrication, system testing, and product analyses were performed on site. The system was composed of stainless steel process units connected by stainless steel tubing. Thermocouples and pressure transducers were placed strategically throughout the reformer system, and data were collected through an on-line data acquisition system.

Catalytic combustion of methanol provided the system heat necessary for reactant vaporization and preheat, as well has for heat of reaction for the endothermic steam reforming of methanol (+50 kJ/mol). The process train is illustrated in Fig. 1. Methanol (from a syringe pump) and compressed air were fed separately to the vaporizer/preheater from which the combined vapor stream entered the combustion zone. Hot combustion gases were then used to heat the steam reformer. Downstream of the reformer, the combustion gases then provided heat to the two vaporizers that fed the combustor and the reformer.

A premixed solution of methanol and water (1:1 ratio by weight) was fed to the system using an HPLC pump. The mixture first entered the reactant vaporizer, then flowed through the steam reformer, where it was converted to H_2, CO_2, and a small amount of CO. The reformate was chilled, passed through a vapor-liquid separator to remove residual water and methanol, and then flowed to the on-line gas chromatograph for analysis.

The gas chromatograph used for these tests is an Agilent Technologies Micro-GC capable of detecting gases and hydrocarbons as large as C_8. However, in the methanol-reforming system, detection of compounds up to C_2 is sufficient. All gases other than H_2, CO_2, CO, and CH_4 remained below the detection limit (100 ppm) of the instrument under the system conditions investigated.

4. Results and discussion

4.1. Combustor demonstration

The combustor used in the system demonstration was first tested as a stand-alone device, and also in conjunction with vaporizers for fuel and water (at flow rates similar to those used in the final device). The main purpose of combustor demonstration was to establish a light-off temperature and investigate effects of equivalence ratios on combustor performance and catalyst life. Light-off temperature is important for both startup and operation. It is the threshold temperature at which the vaporized, preheated methanol, air stream will combust over the catalyst, a temperature that must be achieved using recuperated system heat. In the case of methanol at the conditions investigated, light-off occurred at temperatures as low as 70 °C.

Equivalence ratio (Φ) describes the ratio of fuel to air relative to the stoichiometric ratio, or

$$\Phi = \frac{(F/A)}{(F/A)_{\text{stoich}}}.$$

While Φ values close to 1.0 are desirable to reduce fuel and air consumption, such equivalence ratios place great thermal stress on the combustion catalyst. Therefore, an optimization is necessary in order to protect the catalyst yet operate
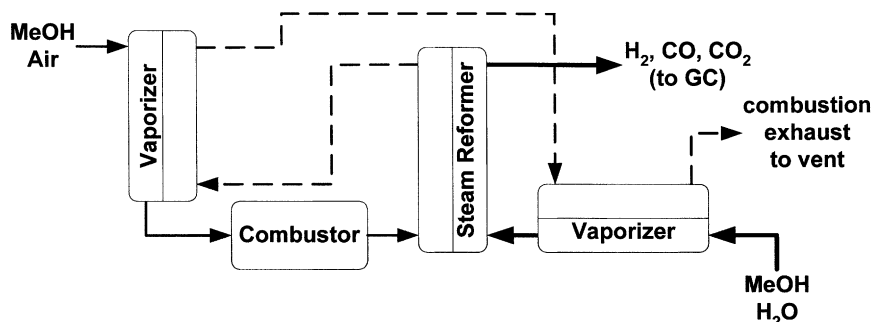

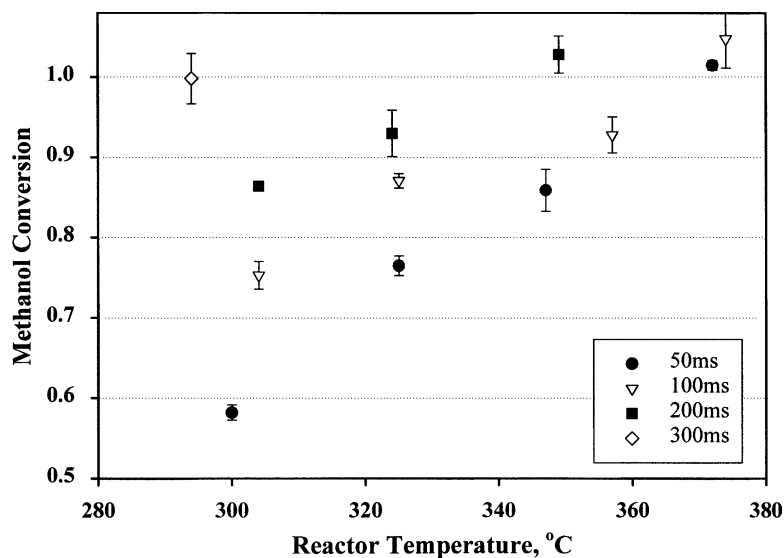Fig. 1. Flow schematic for bread-board methanol steam reforming system.

Fig. 2. Methanol steam reformer: conversion as a function of reactor temperature and contact time (error bars: $\pm 1\sigma$).

the combustor as efficiently as possible. Information on combustor performance versus Φ will be used to determine the size of the catalyst bed in the system combustor as well as the size and power requirements of the system air mover—both important parameters in the final system.

4.2. Steam reformer demonstration

The steam reforming reactor was first demonstrated separately as part of an experimental test stand, where the reactor and vaporizer were electrically heated (i.e. no combustor in system). This allowed the reactor performance to be investigated without introducing other potentially confounding factors. As illustrated in Fig. 2, the reactor was demonstrated over a wide range of temperatures and contact times to obtain performance data. In the final system, an optimum will be reached between these two parameters, based on mission life and the relative importance other factors such as reactor size and operating temperature.

Under the conditions illustrated in Fig. 2, typical dry reformate composition was 73–74% H_2, 25–26% CO_2, and 0.6–1.2% CO. Methane concentrations remained below the detection limit (100 ppm) of the gas chromatograph that was used, as was expected from equilibrium predictions for operation below 400 °C. Methane is formed under certain steam reforming conditions when
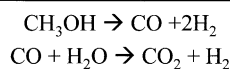
$$3\,H_2 + CO \rightarrow CH_4 + H_2O$$
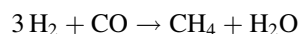
The measured effluent concentrations represent >99.99% selectivity to H_2 and 95–98% selectivity to CO_2.

The low levels of CO (lower than equilibrium) exiting the steam reformer are achievable only with methanol (as opposed to hydrocarbon fuels), and only at low contact times (less than 1 s). This is possible for two reasons. First of all, methanol can be converted through a mechanism that does not involve the water-gas shift reaction, as described by Takahashi et al. [19], and illustrated in Scheme 1. Secondly, short contact times do not allow the secondary (and slower) water-gas shift reaction to occur to an appreciable degree. This effect is enhanced by the fact that the current methanol steam reforming catalyst has very little water-gas shift activity, as shown in other investigations [20]. The net result is a low CO concentration in the reformate because CO is not involved in the mechanism on the right-hand side of Scheme 1. Any CO that does form, therefore, must arise through the reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$).
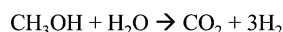
The low concentration of CO exiting the steam reformer provides two major advantages in this methanol-reforming system. First, it increases the hydrogen yield. That is, the theoretical maximum hydrogen yield for methanol steam reforming is 3 mol H_2 per mol MeOH converted. Under these conditions, the hydrogen yield is 2.7–2.8 or 90–93% of the theoretical maximum yield. The second advantage of low CO concentrations is a more simplified CO cleanup. Since current PEM fuel cells cannot tolerate even these low levels of CO, a CO cleanup step must eventually be incorporated into the process train, but a water-gas shift reactor will not be needed.

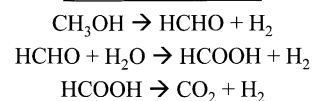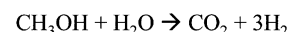| Water-Gas-Shift Mechanism	Alternate Mechanism
$CH_3OH \rightarrow CO + 2H_2$	$CH_3OH \rightarrow HCHO + H_2$
$CO + H_2O \rightarrow CO_2 + H_2$	$HCHO + H_2O \rightarrow HCOOH + H_2$
	$HCOOH \rightarrow CO_2 + H_2$
(CO formed)	*(no CO formed)*
Overall Reaction:	Overall Reaction:
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

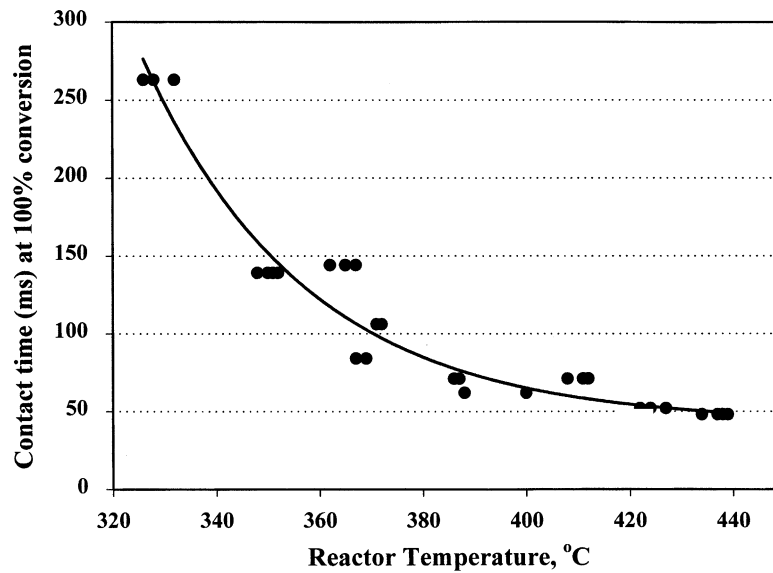Scheme 1. Steam reforming of methanol: alternate conversion mechanisms.

Fig. 3. Methanol bread-board system: contact time versus reactor temperature at complete conversion.

4.3. Bread-board system

The same reactor that produced the results of Fig. 2 was integrated into a "bread-board" (see Footnote 2) system consisting of a combustor, two vaporizers, and a steam reforming reactor. Electric heat was provided to the system for start-up, and after 15 min, electric heat was turned off and the system operated thermally independently for the duration of the experiment. The bread-board system was demonstrated over a range of hydrogen outputs representing 14–80 W_t. The equivalent wattage was calculated assuming no further effluent conditioning (CO clean-up). In the final system, the hydrogen-rich effluent will be fed to a PEM fuel cell with an expected energy efficiency of 60% and a hydrogen utilization rate of 80%. Based on these assumptions, the equivalent electric output of the processor is equal to 48% of the thermal wattage of the hydrogen produced.

Fig. 3 illustrates the operating conditions under which >99% conversion of methanol is attained in the bread-board configuration. As expected, longer contact times (lower throughput) are necessary at lower operating temperatures. A system analysis will be performed to determine the optimal balance between contact time and temperature for the final integrated system. For instance, higher operating temperatures may allow for smaller reactor volumes, but they also increase the need for insulation, which would add bulk. At such small device sizes, bulk may ultimately be more important than mass, so there is likely to be a trade-off between reactor volume and insulation volume.

Fig. 4 shows thermal efficiency of the bread-board device as a function of device power. Heat recovery and insulation issues have not yet been fully addressed, so the current process train represents a worst-case scenario. System efficiency increases sharply with power from 14 to 60 W_t, where it levels off to a constant value of ~58% at higher

power levels. This again shows the significance of the line losses in the bread-board system, which were found to consume more than 40% of the combustion heat generated in the system. More significant conduction losses at the lower power levels would be expected, since the system has the same surface area regardless of the power level at which it is operating.

A base case set of operating conditions was chosen to demonstrate not only efficiency, but also energy density and total fuel weight for 3-day and 14-day missions. As listed in Table 4, the base case operating conditions were 350 °C reactor temperature, 140-ms contact time, and a steam to carbon ratio of 1.8:1. Under these conditions, methanol conversion was >99%, and the system produced 27 W_t of hydrogen. Processor efficiency was then calculated, based on the lower heating value (LHV) of fuel fed to the system and the LHV of hydrogen produced, resulting in a fuel processor efficiency of 45%. Based on the previously mentioned fuel cell efficiency assumptions, the complete fuel processor/fuel cell system would produce 13 W_e at an overall efficiency of 22%.

For the base-case conditions, dry gas composition was 74% H_2, 25% CO_2, and 0.8% CO. Any methane produced during base case operation was below the detection limit (100 ppm) of the gas chromatograph. The very low CO concentration of the reformate eliminates the need for a water-gas shift reactor, significantly simplifying the overall system.

The energy density of the bread-board system for the base case (and a 14-day mission) was 720 Wh/kg, a level that is already several times higher than the best lithium-ion battery. Even a 3-day mission would yield an energy density greater than the expected energy density of future lithium-ion batteries (300 Wh/kg). There are several obvious areas which, if addressed, would significantly raise the efficiency and energy density of the system. For instance, as mentioned
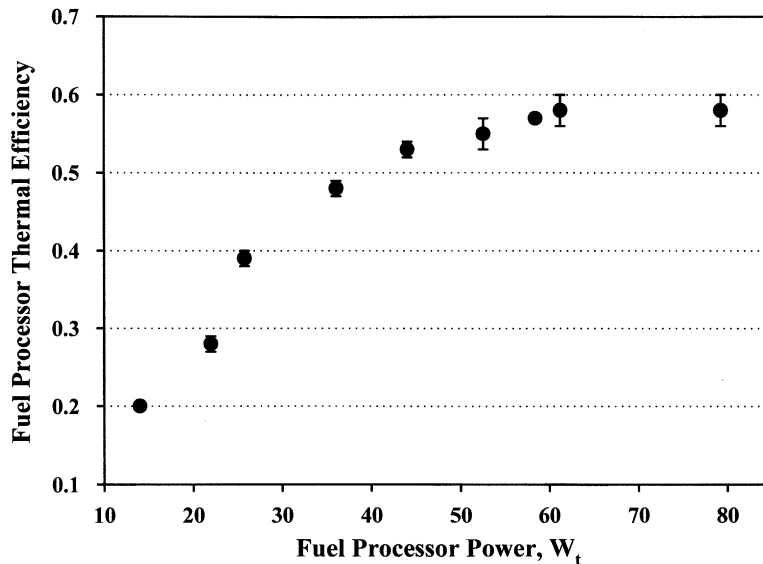
Fig. 4. Methanol bread-board system: thermal efficiency versus system power (error bars: ±1σ).

Table 4
Base case demonstration results

Operating conditions		
Reformer temperature	350 °C	
Contact time	140 ms	
Water/MeOH molar ratio	1.8	
Fuel processor results		
MeOH conversion	>99%	
Gas composition		
H_2	75%	
CO_2	24%	
CO	0.8%	
Hydrogen production	27 W_t	
Methanol fed to system (reformer and combustor)	60 W_t	
Fuel processor efficiency	45%	
Fuel Cell power estimate[a]	13 W_e	
Fuel processor/fuel cell system efficiency[a]	22%	
Estimated system energy density[b]	14-day mission	720 Wh/kg
	3-day mission	450 Wh/kg

[a] Assuming fuel cell efficiency of 60% with 80% H_2 utilization.
[b] Assuming a 1-kg fuel processor/fuel cell system.

earlier, line losses and exhaust heat were found to consume more than 40% of the combustion heat produced in the system. Eliminating these losses alone would increase the base case fuel processor efficiency to 60% and its energy density to 870 Wh/kg.

5. Conclusions and future work

A 15-W_e bread-board methanol fuel processor has been developed for portable power applications. The current reactor train includes a combustor, two vaporizers and a steam reforming reactor. The device has been demonstrated under thermally self-sufficient conditions over the range of 14–80 W_t.

Assuming a 14-day mission life and a 1-kg fuel processor/fuel cell assembly, a base case was chosen to illustrate the expected efficiency and energy density of the system. Operating at 13 W_e, the system has a fuel processor efficiency of 45% and an estimated overall efficiency (including fuel cell) of 22%. This translates to an energy density of 720 Wh/kg, which is several times the energy density of the best lithium-ion batteries. Some immediate areas of improvement in thermal management also have been identified, and these will be addressed as the system is more fully integrated.

The final power system will be a hybrid, containing a fuel reformer, a fuel cell, and a rechargeable battery. The battery will provide power for start-up and added capacity for times of peak power demand.

Development will continue with the integration of the bread-board parts into a single compact unit. This is expected to greatly increase system efficiency and ultimate energy density. Other future work includes investigations of steam-to-carbon ratio and CO cleanup, as well as the incorporation of suitably sized peripherals as they become available.

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