COMPACT FUEL PROCESSORS FOR PEM FUEL CELLS

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Introduction

Recent improvements in the design and manufacture of PEM fuel cells have increased interest in their use as a replacement for batteries and other, larger power supplies (e.g., internal combustion engines). Although PEM fuel cells represent a relatively mature technology (they have been around since 1839), they have yet to receive widespread commercial or military use primarily due to the non-availability of reliable, convenient, and compact hydrogen sources. Several approaches have been identified for hydrogen generation and/or storage. These include hydrocarbon and methanol fuel reforming, hydrogen absorption into metal hydrides, hydrogen-generating chemical reactions, and ammonia decomposition (Blomen and Mugerwa, 1993; Bloomfield et al., 1995). We have developed a compact ammonia-processing MesoChannel™ reactor system that generates hydrogen at a rate sufficient to meet the requirements for a 50 W PEM fuel cell. More recently, we have extended the capabilities of our hydrogen generator to process C_1 to C_4 hydrocarbon fuels. A summary of our work on compact fuel processors is the subject of this paper.

Hydrogen from methane

Compact hydrocarbon-based hydrogen generators are needed to power a wide range of portable applications. Our target was to produce hydrogen at a rate sufficient to power a 20 W PEM fuel cell to satisfy the requirements of our subcontract to the Research Triangle Institute under the Defense Advanced Research Projects Agency (DARPA) Palm Power Program. The hydrocarbons to be evaluated under this project include butane and JP-8. Since steam reforming of these higher hydrocarbons proceeds through the reformation of methane, we decided to first evaluate the steam reforming of methane using our MesoChannel™ reactor. The hydraulic diameters of the channel in these reactors were in the 0.5 to 1.5 mm range as opposed to the micron sized channels that are typically adopted in micro reactors.

Methane (C.P. grade) and other gases such as hydrogen (commercial grade) for pretreatment of the catalysts were metered through Brooks 5850E mass flow controllers. Distilled water was vaporized at 180 to 250 C. Methane and the steam generated in a vaporizer were contacted downstream of the vaporizer and were then routed through a preheater. The steam-hydrocarbon mixture was heated to within 50 C of the desired reaction temperature in the preheater. The reaction temperature was typically in the 550 C to 625 C range. Temperatures were measured using Inconel-clad 1/16 inch OD type K thermocouples. The gas mixture exiting the preheater was routed into the MesoChannel™ reactor. The gases exiting from the reactor passed through a back pressure regulator and into a condenser to remove any unreacted water, and the dry gas mixture was vented or combusted before venting. The flow rate of the dry product gas was monitored continuously. A portion of the dry gas was routed to a gas chromatograph (Shimadzu GC 17A) for analysis. The gas chromatograph was equipped with a flame ionization detector, a methanator and a thermal conductivity detector. The carbon balance was found to be within 3%.

Figure 1 shows the hydrogen production rate observed while operating in the 600 to 625 C range and at residence times of less than 0.4 s.

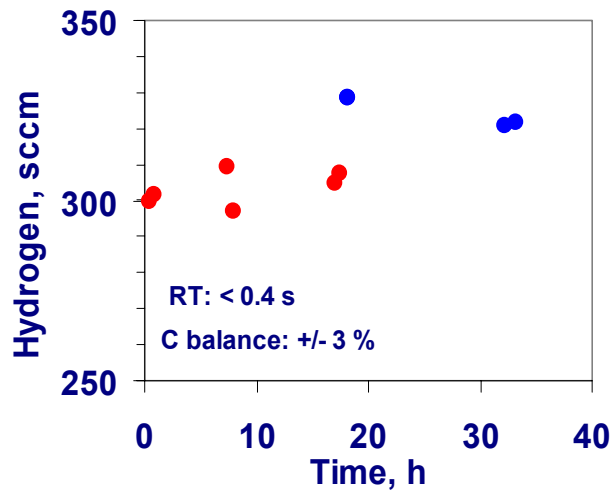

Figure 1. Hydrogen generation-steam reforming of methane. 600 C (red), 625 C (blue).

As can be seen, excellent catalyst stability was observed for over 30 h. The methane conversion during this period was about 53 % (equilibrium conversion at 625 C, S/C ratio of 1 is about 85%). As shown in Figure 2, the product stream contained only about 5% CO during this period.

Our next efforts will target the integration of hydrogen separation schemes into the reactor. The reactor will be modified to accommodate a combustor that is in close proximity to the reformer (similar to our ammonia cracker system that is discussed below). Unreacted methane and/or hydrocarbons will be combusted to drive the reforming of hydrocarbons.

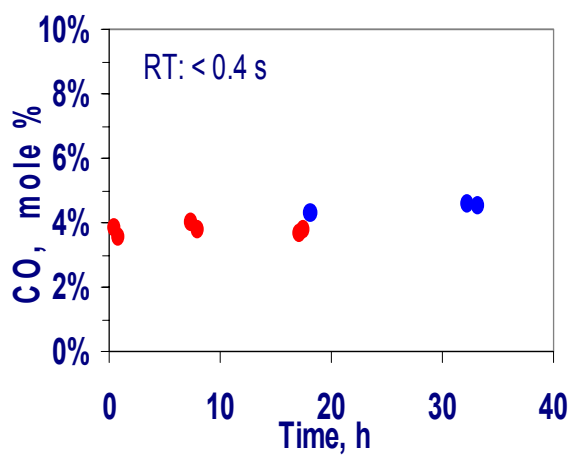

Figure 2. CO content in the product gas (dry basis). 600 C (red), 625 C (blue).

Hydrogen from ammonia

Ammonia decomposition for PEM fuel cell applications has received relatively less attention because of ammonia's toxicity and foul odor, and because it is not economical for power production except in remote, low-power applications (Appleby and Foulkes 1989). Of greater significance is the fact that trace ammonia needs to be effectively removed before the product stream is fed to the PEM fuel cell. However, ammonia is an attractive source because the usable hydrogen per kilogram of fuel is relatively high (Figure 3), particularly when the weight of water needed for hydrocarbon steam reforming is taken into account. Stoichiometric steam/fuel ratios were assumed in Figure 3.

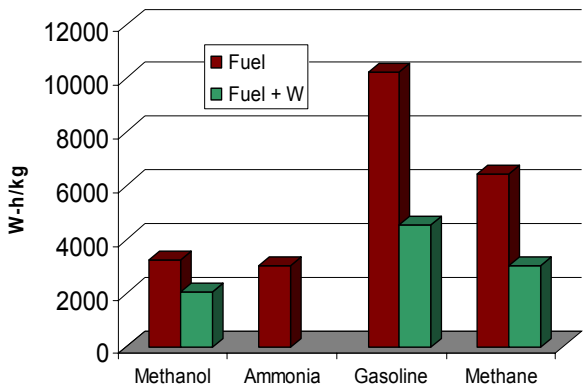

Figure 3. Comparison of fuels: Energy density.

Ammonia decomposition was conducted in MesoChannel™ reactors. The reactor volume and weight was typically less than 4 cc and less than 140 g, respectively. The reactor is integrated with a heat exchange system in an elegant and rugged fashion that is suitable for field use. Our current prototype produces hydrogen at a rate sufficient to generate 50 W of electrical power from a fuel cell, providing up to 1000 W-h of energy. The prototype, which is named MAC-50 (MesoSystems Ammonia Cracker), has the options of either providing heat by hydrocarbon combustion (typically butane) or by combusting ammonia itself. The combustor contains a versatile catalyst-coated substrate that also allows for quick start-up.

The MAC-50 system includes the following design features that serve to minimize size and weight:

- MesoChannel™ reactor architecture to minimize heat and mass-transfer limitations so reactor sizing is driven by the catalyst's intrinsic kinetics and is thereby minimized
- Use of a high-activity noble metal catalyst to keep reactor volume small
- Lightweight, recuperative heat exchanger to improve the system thermal efficiency and reduce the quantity of fuel that must be burned to maintain the reactor at temperature
- Lightweight, ultra-low-thermal-conductivity insulation to reduce heat loss to ambient without significantly increasing the system size
- Butane/propane and/or ammonia combustion for rapid reactor startup and to provide heat during steady-state operation.

Figure 4 shows the performance of our catalyst for ammonia decomposition over a 300 h testing period. This duration also includes 6 thermal cycles between room temperature and 600 C. As can be seen, the catalyst showed excellent activity and stability over this period.

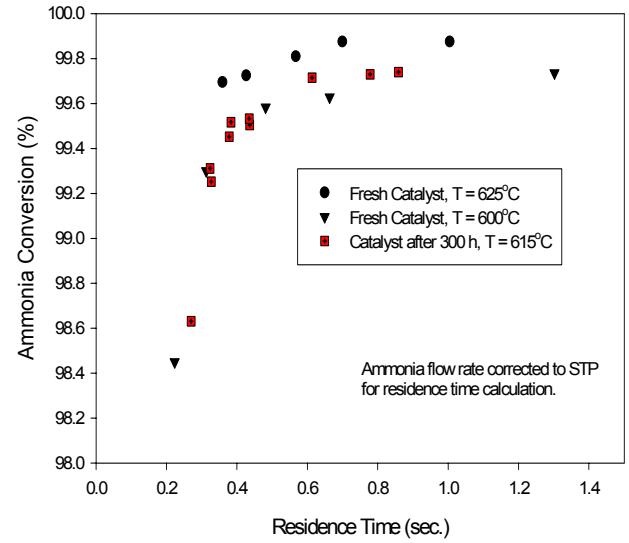

Figure 4. Stability of catalysts to ammonia cracking.

A photograph of the MAC-50 prototype is shown in Figure 5. The prototype includes the reactor, recuperators, and an adsorbent column. High-temperature vacuum insulation is used to limit the heat loss to the surroundings to less than a 2 W at 600C. The system mass is about 820 grams, not including the ammonia. The 0.8-liter ammonia storage tank will hold up to 480 grams of anhydrous ammonia, which will yield about 1150 W-h of energy from a fuel cell (assuming 17 W-h per gram of hydrogen). Roughly 20% of the ammonia is consumed in the combustor and 80% is fed to the decomposition reactor. Including the mass of the ammonia, this prototype produces hydrogen with an apparent energy density of about 1150/(820+480) = 885 W-h/kg.

Figure 5. MAC-50 Prototype.

The product typically contains about 2000 ppm of residual ammonia. Since ammonia is harmful to PEM fuel cell performance, the residual ammonia is completely removed using a proprietary high capacity carbon adsorbent. A typical breakthrough curve of the adsorbent that was obtained while using 0.7 SLPM of air containing 1000 ppm ammonia is shown in Figure 6. The adsorbent (30 g used for the test in Figure 6) has a capacity of about 9 to 10 wt.-% and as a result, the MAC-50 prototype needs only about 30 g of adsorbent for a 1000 W-h duty. To put this in perspective, the capacity of commercial adsorbents is in the 2 to 4 wt% range.

We are now in the process of field testing the MAC-50 prototype after integrating it with a PEM fuel cell. Based on the results of these tests, a control system will be designed and incorporated that would allow for quick start-up and shut-down as well as load following capabilities.

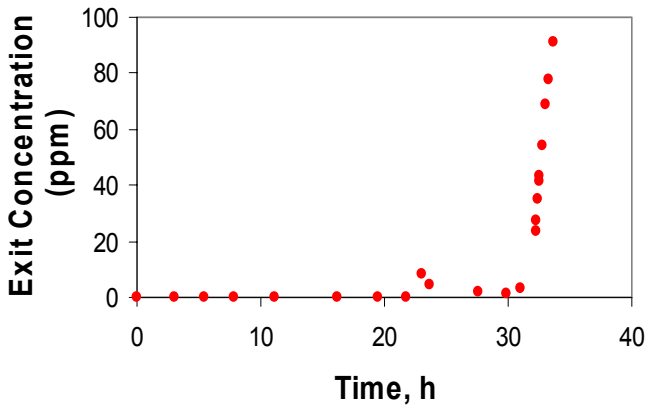

Figure 6. High performance ammonia adsorbents: Breakthrough curves.

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