Microplasma Reforming of Hydrocarbons

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Abstract: Portable fuel cells are attractive alternatives to batteries because of their high specific energy density. One of the key obstacles to fuel cell implementation is a ready source of hydrogen. Hydrogen gas is impractical because of its low density even when compressed. A more practical approach is conversion of hydrocarbon fuels to hydrogen through a reforming process. Catalytic reforming systems have a number of limitations such as poisoning, coking, coarsening, long start-up times and excessive costs. Published studies have shown the viability of plasma reforming but none have succeeded in achieving suitable system efficiencies for portable applications. Efficient, atmospheric pressure, non-thermal microplasmas hold promise as a hydrocarbon reforming technology that can circumvent catalytic reforming issues and improve on conventional plasma reactors. This work presents results on the feasibility of microplasma hydrocarbon reforming. To date, microplasma reactor devices have been designed, fabricated and characterized under diverse process conditions. Recent experiments involving microhollow cathode reactors achieved hydrocarbon conversions up to 42%. We have also begun to characterize the energy balance on the microplasma reforming devices and report experimentally measured efficiencies.

Keywords: Microplasma, Reforming, Hydrocarbons, Portable Fuel Cell, Methane

1. Introduction

Today’s technology driven world requires portable power systems that are reusable, environmentally friendly and high in energy density. Fuel cells can meet these requirements, but the limitation of an available supply of hydrogen makes them impractical for portable applications. Hydrogen is commonly supplied by reforming hydrocarbons at industrial facilities, but issues’ surrounding safe storage and transportation of hydrogen has prevented the realization of portable fuel cells systems. Our ultimate goal is to demonstrate the feasibility of a microplasma reforming device to potential provide hydrogen on site.

Though catalytic reforming of hydrocarbons is a popular method, it has many drawbacks that are problematic for portable applications. For example, sulfur components common in fuels poison catalyst, coking blocks catalytic sites, and catalytic processes often operate at high temperatures resulting in long start-up times [1]. These issues have been addressed and optimized in large scale facilities, but are still factors in portable reforming applications. Although plasma reformers circumvent these limitations, their implementation has been restricted due to low system efficiencies [2]. Microplasmas (plasmas in sub-mm geometry), possess high electron densities and a relatively high fraction of energetic (> 20eV) electrons which are theoretically able to efficiently promote chemical reactions [3]. This research attempted to capitalize on the advantageous properties of a microplasma including the convenience of its miniature size to produce hydrogen for portable fuel cells.

2. Methods and Materials

The microplasma reactors used in these experiments operate with a non-thermal plasma and are ignited using either a direct current or pulsed DC power supply (<80 kHz). The device is a microhollow cathode discharge (MHCD) with an elongated
trench. The MHCD design is appealing as it has an increased electron density even relative to other types of microplasma devices. The increase is due to the oscillation of electrons between each cathode wall, known as the Pendel effect [4]. The device was fabricated using microelectromechanical systems (MEMS) techniques. The microplasma reactor substrate is n-doped silicon, the dielectric is silicon dioxide which was thermally grown on the silicon surface and thenpatterned and etched. The anode is nickel on a titanium adhesion layer and the cathode is the silicon substrate with a resistivity of 5 Ω-cm. A thin layer of titanium and gold is deposited onto the backside of the cathode to ensure electrical connectivity.

Figure 1. Cross Section of Microplasma Device [5,6]

According to Paschen’s law the breakdown voltage is directly linked to the electrode distance, \( d \), and the pressure of the gas, \( p \) [7]. For a given gas there is a minimum breakdown voltage for a specific \( pd \) value. Common values of \( pd \) for minimum power plasma operation are around 10 to 100 torr-mm, depending on the gas. Aiming to minimize the power required to sustain the plasma at atmospheric pressure the device was designed with electrode distances between 2 and 250 microns. Further description of the device can be found in previous publications [5,6,8].

The fuel and the carrier gases were fed to the microplasma reactor from individual mass flow controllers (Aalborg, Inc.) at various flow rates. Plasma developed within the channel of the device by applying electrical power. The products of the microplasma reaction were then fed through a two position sample valve (Valco Instruments Co. Inc.), to send a 50 microliter sample to a micro gas chromatography unit (Varian CP-4900) approximately every two minutes. The output was fed to a quadropole mass spectroscopy (Stanford Research Systems QMS200). The GC and the QMS were used to determine the mass balance of the reaction. The power into the microplasma device was monitored with an oscilloscope (Tektronics TDS 2014B) and data acquisition units (National Instruments USB 6008). The temperature within the microplasma holder was monitored to help determine the energy balance.

Figure 2. Experimental Setup [5]

Fuels tested for these experiments were volatile hydrocarbons such as methane. Methane, as a reactant, should only produce a limited variety of components during a reforming process, simplifying the mass balance. Also, methane has a high carbon-hydrogen bond dissociation energy which can serve as an indication of how reforming might proceed with larger more complex alkanes [9].

The carrier gas used was nitrogen. Initial experiments with pure hydrocarbons displayed stable microplasmas but did not result in conversion. The presence of nitrogen facilitated a plasma decomposition reaction, as consistent with reports elsewhere which suggest that the excitation of nitrogen into higher vibrational and metastable states aides in the reforming process [10]. Nitrogen is also a practical choice due to its abundance in the air.

To date multiple experiments tested with these devices demonstrate microplasma activated hydrocarbon decomposition.

3. Results and Discussion

An example of an experiment with pulsed DC power is illustrated in figure 3. Based on composition,
flow and thermal data we determined mass and energy balances.

As observed, the initiation of the microplasma quickly leads to the increase of the hydrogen peak and the decrease of the methane, showing conversion. Also, the low background concentration of oxygen decreased as water and carbon dioxide signals increased indicating undesirable side reactions.

A reforming reaction deduced from the mass balance of a representative methane reforming experiment is shown as follows:

\[
\begin{align*}
1.000 CH_4 + 0.049 O_2 & \rightarrow 1.659 H_2 + 0.694 C_3 \hspace{1cm} (1) \\
+0.106 C_2 H_2 + 0.096 H_2 O + 0.046 C_2 H_6 + 0.001 CO_2
\end{align*}
\]

The reaction in equation 1 produces 1.659 moles of hydrogen for every mole of methane reacted. This is an indication that the hydrogen generated is a combination of methane decomposition, equation 2, and acetylene generation, equation 3.

\[
\begin{align*}
CH_4 & \rightarrow C(s) + 2H_2 \hspace{1cm} (2) \\
CH_4 & \rightarrow 0.5C_2 H_2 + 1.5H_2 \hspace{1cm} (3)
\end{align*}
\]

These experiments also demonstrate the ability to generate hydrogen without producing oxides of carbon, an extremely attractive result in light of environmental concern. Although a minuscule amount of carbon dioxide is formed in equation 1 this can be completely avoided by removing residual oxygen in the fuel.

For the overall reaction the enthalpy was calculated to be 71.36 kJ/mole. This is an endothermic reaction indicating that the temperature rise during the experiment is a product of joule heating. The energy balance is then determined through the conservation of energy.

\[
\sum_i \left( m_i \dot{H}_i \right)_{in} - \sum_j \left( m_j \dot{H}_j \right)_{out} + P_{in} + \dot{Q} = (mC_p)_{sys} \frac{dT}{dt} \hspace{1cm} (4)
\]

In this case the energy inputs are in terms of instantaneous electrical power, enthalpy in, and heat from the surroundings to the system. For these experiments the heat is lost from the system and is therefore a negative value. The energy out of the system is calculated from the enthalpy out and the accumulation of energy is determined by the storage of sensible heat in the system.

The energy balance is established by integrating the terms in equation 4 over the period of time that the device is operational. For example, the electrical energy into the system can be determined by...
integrating the instantaneous power, $P_{in}$, over the entire run. The energy accumulated by the system is calculated from the slope of temperature over time.

The value for heat loss was established by looking at the temperature versus time curve after the device had been turned off but with gases still flowing. For this section of time there is no electrical power into the system and the enthalpy changes are negligible. This allows the energy balance to take the form shown in equation 5.

$$\dot{Q} = (mc_p)_s \frac{dT}{dt}$$

By equation 5 the heat loss rate can be calculated as a function of temperature. This term can then be used in equation 4 as an expression of the heat loss rate when the plasma is ignited.

To date experiments have shown that only 1 to 2% of the electrical energy into the system represents the reaction enthalpy for the reforming process. This is primarily due to energy conversion into heat. By insulating the system the un-captured heat can be harnessed to drive the thermodynamic equilibrium towards the products. The heating effects can also be minimized through the use of pulsed power and additional improvements in device structure.

4. Conclusions and Future Work

These initial reforming experiments show the feasibility of an eventual microplasma fuel reformer-fuel cell system. Although the percentage of power used for the reaction is relatively low the process has not been optimized and is on the same order of existing optimized plasma devices [11]. Further work is required to increase the efficiency of the reaction, process and overall system. Minimizing the amount of gas that circumvents the microplasma would improve the reaction conversion and hydrogen yield significantly.

Research into reforming larger hydrocarbons is also crucial as they possess greater energy densities by volume and weaker carbon-hydrogen bond strengths. This suggests the possibility of a higher conversion rate and an increase of hydrogen production. This research also motivates additional studies to better understand how operating conditions affect conversion and energy efficiencies. Furthermore, this microplasma device could potentially be used for a variety of chemical reactions and applications beyond reforming.

Acknowledgements

The authors wish to acknowledge the assistance and support of Sang Youp Hwang, Nathan Meryash, George Wohlrab and Bruce Fraser. The support of the National Science Foundation under grant no. NSF DGE-0742462 and the Army Research Office under grant no. W911NF-07-1-0118 are gratefully acknowledged.

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