

NON-THERMAL MICROPLASMA REFORMING OF HYDROCARBONS

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Background

Environmental and efficiency problems of combustion energy production have made fuel cells extremely popular as a current topic of alternate energy research. The major limitation of hydrogen fuel cell systems is the lack of a readily available stream of hydrogen. Hydrogen requires large volumes due to its low energy density (11 kJ/L) and is highly combustible. Hydrocarbons are generally converted into a hydrogen rich stream through the reforming process. Traditional catalyst reforming processes have been used, but problems due to high device weights, catalyst poisoning issues, long start up time and excessive costs often make them impractical for commercial use [1-3]. Through the use of an efficient, non-thermal microplasma a hydrocarbon reforming system can be developed that circumvents current catalyst reforming issues.

The United States Army can potentially use microplasma technology to reform JP-8, a readily available military fuel and provide hydrogen to power fuel cells. This is beneficial as current portable power sources are supplied by battery power, which in large quantities can become too burdensome for the soldier. Furthermore the production demands to supply these batteries cannot always be met. An example of this was illustrated during Operation Iraqi Freedom in 2003 when the standard BA5590 battery (20 W, 154 W-hr) was in such short supply that six manufacturing plants working continuously could not meet demand [4]. Reforming JP-8 with microplasmas would develop a long-life, efficient, portable, reusable 'fuel processor-fuel cell' system, reducing the strain of battery technology in the military.

Introduction

The advantages of plasma reforming over catalyst reforming have motivated several research efforts in recent years. There have been various experiments published in literature using plasma as a reforming media for hydrocarbons like diesel, oil, gasoline, JP-8, methane and natural gas among others [1, 2, 5]. These investigations have shown the promise of plasma reforming, but have experienced issues achieving suitable system efficiencies. This project intends to show that microplasmas have advantages in comparison to catalyst, and offer overall improved system efficiency in comparison to conventionally-sized plasmas. This overview introduces the characteristics of plasma as a form of matter, the application of plasma as a reforming technology, and the theoretical benefits of non-thermal and micro-scale plasma operation.

Plasma

Plasma, the fourth state of matter, is defined as a neutral collection of ionized gas species and is the most abundant form of matter in the universe. Some examples include the sun and stars, the aurora borealis, lightning, fire and other such natural phenomena. There are also many every day examples of industrial and commercial plasmas. Items such as plasma TVs and fluorescent lights have found their way into homes and businesses. Industrial uses for

plasma have been used for arc welders and plasma torches [6, 7]. Plasma technology has also been developed to etch and produce small, fine features prevalent in semiconductor fabrication.

Advantages of Plasmas Reforming over Catalysts Reforming

A chemical reaction occurs when a reactant converts to a product. The Arrhenius equation (Equation 1) governs the rate constant of a particular chemical reaction.

(1) **Arrhenius Equation** [8]:
$$k = Ae^{-\frac{E_a}{RT}}$$

The dependence of the rate constant, k , is primarily due to the temperature and the activation energy of the reaction. Plasmas do not normally affect the overall activation energy of a chemical reaction, but rather they increase the temperature of reactive species and electrons reaching temperatures from 1 to 10eV (11,600 to 116,000K). The presence of high temperature electrons in the plasma diminishes the effect of the activation energy, and potentially offers a nearly instantaneous reaction rate. Catalysts are typically used to increase the rate constant via a reaction pathway with lower activation energy as shown in Figure 1.

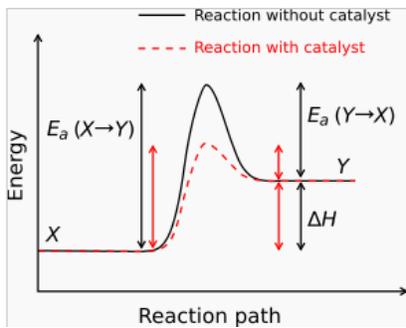


Figure 1. Reaction Path [9]

On the other hand, catalyst-based reforming processes have three major limitations; sensitivity to sulfur compounds, adverse effects of carbon deposits due to coking, and a long start-up time. Sulfur compounds cannot be tolerated at even minuscule concentrations as it acts as a poison blocking active catalyst sites. In particular, JP-8 fuel is known to contain sulfur levels up to 5000 ppmw [3, 10]. Catalytic reforming of JP-8 requires high operating temperatures exceeding 800°C, and would still be susceptible to poisoning from a monolayer of sulfur [3]. To avoid poisoning the catalytic reformer, the fuel requires a separate hydrodesulphurization (HDS) reaction. The HDS reaction converts sulfur compounds into hydrogen sulfide (H₂S). H₂S is then removed using a zinc oxide (ZnO) absorber. The addition of the HDS step not only complicates the system, but also necessitates an additional feed stream of hydrogen (Figure 2). An additional problem with catalysts is coking. Coking is the deposit of solid porous carbon or ash. Coke deposits result in a reduction of available active sites leading to overall catalyst deactivation. Carbon deposits are frequent when breaking down large carbon chains. Coking renders catalytic reforming ill-suited for hydrocarbon reforming processes. Furthermore, the start-up time for a catalytic reformer could take several minutes, rendering a power system useless during the start-up period [2].

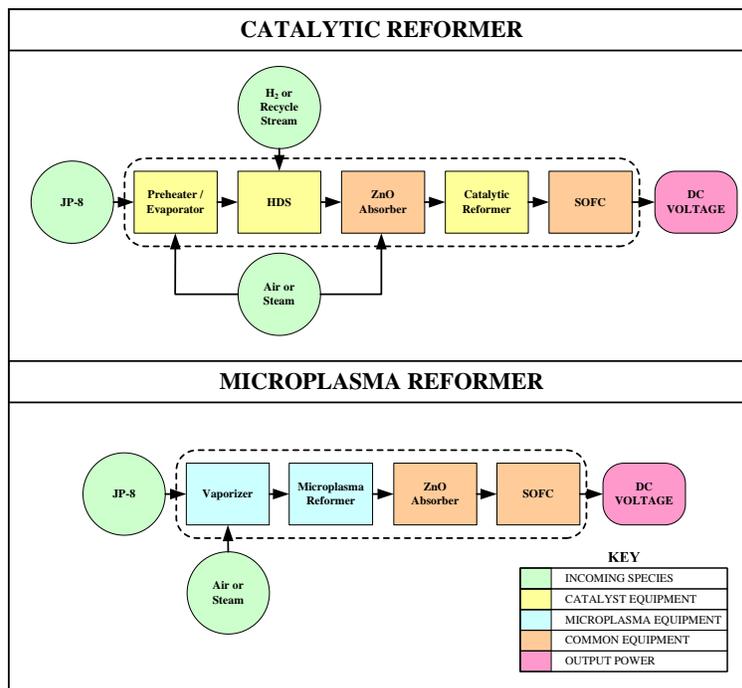


Figure 2. Comparison of Catalyst Reforming and Microplasma Reforming [11]

Plasma technology essentially avoids all of these issues. Earlier work demonstrated that plasmas can break down sulfur compounds present in hydrocarbon fuels, eliminating the need for the HDS step. This was observed in work at Stevens Institute of Technology in collaboration with FuelCell Energy Inc. of Danbury, CT [12, 13]. For this experiment NATO F-76 logistical fuel was sent through a non-thermal plasma device and a significant fraction of the organic sulfur components were converted into H_2S . Although coking is not expected to slow the reaction rate, the effect of coking on the microplasma device has not yet been investigated. Finally since the plasma is controlled through its own power supply, the start up of the device is instantaneous, determined only by the input power. For these reasons, we propose to further explore plasma technology, especially non-thermal, micro-scale plasma devices as a potential reforming mechanism for large hydrocarbon fuels.

Advantages of Non-thermal Plasmas

Thermal plasmas are defined as having electrons and the medium gas at the same temperature. Non-thermal plasmas occur under much lower electrical power, around only a few hundred watts. This process is defined as the electrons being at a much greater temperature while the surrounding medium remains at room temperature. Non-thermal plasmas do not provide significant energy to the system as thermal plasmas do, but they generate radicals. Non-thermal plasmas are ideal for chemical reactions due to their low temperature. They allow the energy consumption to be much lower, minimize electrode erosion and minimize the overall size and weight of the device [2].

Advantages of Microplasmas

Plasma technology therefore provides a non-equilibrium environment in which the generated, chemically-reactive free radicals promote chemical conversion and offer interesting prospects for hydrocarbon reforming [2]. The application of plasmas to reforming processes has recently been studied under various conditions but efficiency issues remain. At MITs Plasma

Science and Fusion Center (PSFC) a non-thermal plasma reactor called a plasmatron was tested with various fuels. Although very successful in chemical conversion, the device could not produce energy efficiencies beyond 74% [5]. Providing higher electron and free radical densities should theoretically increase the overall efficiency.

A plasma confined to at least one dimension 1 mm or less defines a microplasma [14]. As an emerging field of low temperature plasma science and technology microplasmas have much higher power densities (exceeding 1 kW/cm^3), higher electron densities (exceeding 10^{15} cm^{-3}) and increased surface-to-volume ratios when compared to conventional, large-scale plasma-chemical systems. A high surface-to-volume ratio imparts excellent thermal management and mixing characteristics that help maintain homogeneous, isothermal reacting volumes [15]. These microplasma characteristics present processing advantages for hydrocarbon reforming applications.

Moreover, conventional plasma processes generally operate at lower pressures allowing the system to meet the Paschen Minimum, minimum breakdown voltage. Table 1 shows the minimum breakdown voltage for various gases and the ideal electrode distance, d , for atmospheric pressure. Processing with microplasmas makes operating at atmospheric pressures possible due to the small distance between electrodes. Operating at atmospheric pressure minimizes equipment requirements and simplifies the overall operating system.

Table 1. Minimum Sparking Constants for Selected Gases [16]

Gas	Cathode	$V_{b, \text{min}}$ (Volts)	pd_{min} (10^{-3} Torr-m)	$d_{\text{min @ 760 Torr}}$ (μm)
Ag	Fe	265	15.0	19.7
Air	-	360	5.7	7.5
CO ₂	-	420	5.0	6.6
H ₂	Pt	295	12.5	16.4
He	Fe	150	25.0	32.9
Hg	W	425	18.0	23.7
Hg	Fe	520	20.0	26.3
N ₂	Fe	275	7.5	9.9
N ₂ O	-	418	5.0	6.6
O ₂	Fe	450	7.0	9.2
SO ₂	-	457	3.3	4.3

Microplasma technology offers many advantages in the devices design. They are generally small and can be designed to be any shape. The devices can easily include micro fluidic connections to allow for a flow through process. Integrated electrodes and heat exchangers for the individual microplasma devices are possible. Scaling up from experimental setup to the final design is simple as the reactors would have the same dimensions. Moreover micro fabrication devices are relatively inexpensive to produce. These advantages make microplasmas ideal for a portable hydrocarbon fuel reforming process.

Research Accomplishments

To date microplasma reactor chips have been designed and fabricated having different channel geometries using silicon microfabrication technology at the Cornell Nanofabrication Facility of Cornell University in Ithaca, New York. The microplasma reactors produced are microhollow cathode (MHC) devices with a variety of geometries.

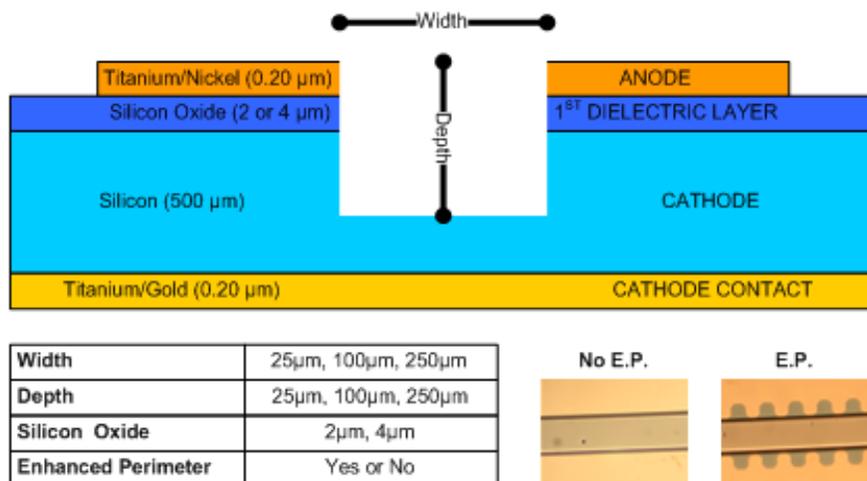


Figure 3. Microhollow Cathode Devices

After the fabrication of the microplasma reactors, a vacuum chamber was assembled to allow for testing and verification of plasma behavior. Initially tests were done with various inert gases such as helium, neon and nitrogen. To date inert plasma experiments have shown our devices to be comparable to literature. We have also observed the effects of device geometry and the degradation of the devices. Experiments were tested using the setup shown in Figure 4.

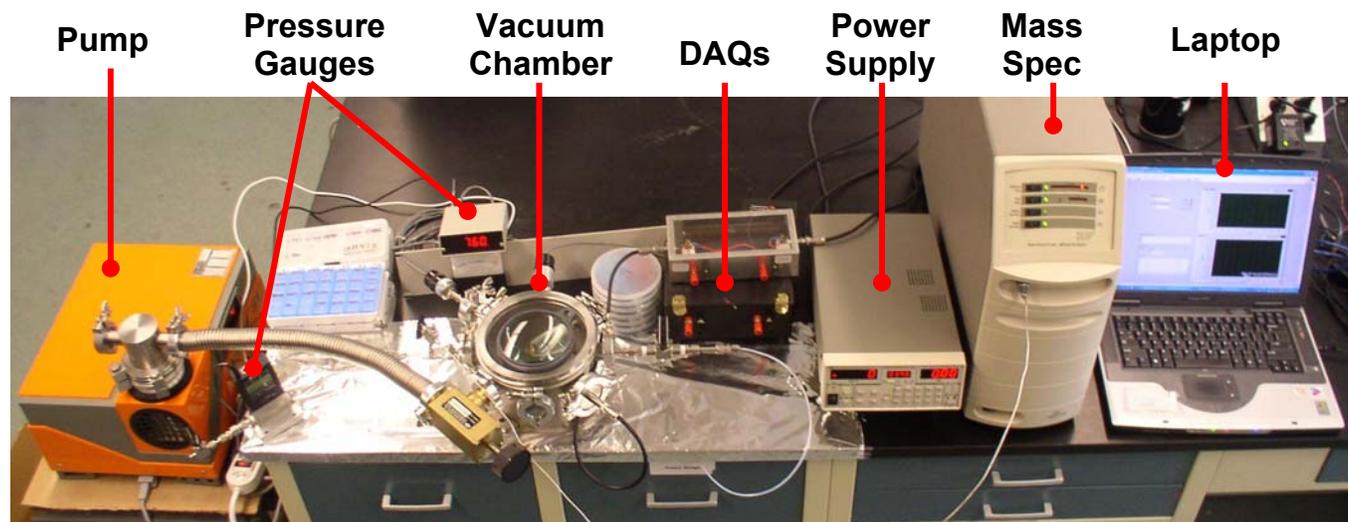
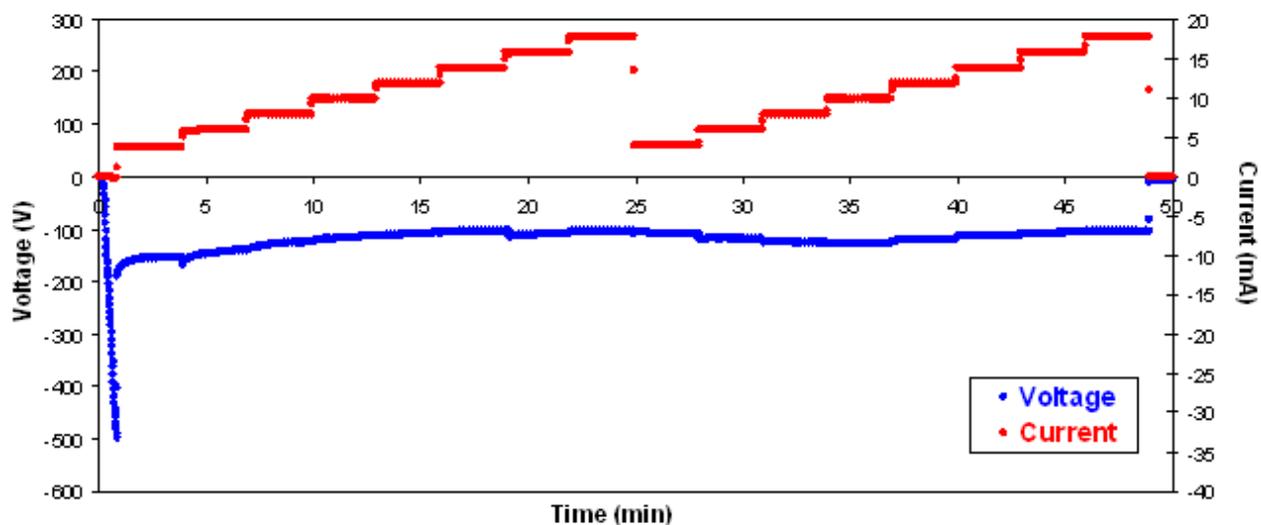


Figure 4. Experimental Setup

Developing butane plasma began our work on volatile hydrocarbons. Butane experiments gave promise to developing a plasma with hydrocarbon fuels. Experiments with butane determine the effects of microplasma device geometries.

Results

Butane has been tested with various geometries to determine the effect of the device. Tests were done by limiting the applied current while monitoring the current and voltage. These tests sustained point plasmas of butane that exceeding power densities of $10\text{MW}/\text{cm}^3$. Figure 5 shows an example of data from a butane plasma experiment.



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Figure 5. Microplasma Butane at 760 torr

These experiments give us the ideal dimensions for the second generation micro fluidic reactors.

Additional tests to seal the current plasma devices have shown varying effects that must be developed to be reliable prior to the next evolution of the microplasma reactor. Second-generation enclosed microplasma reactors will allow for a continuous feed-flow reaction while concealing the plasma. These reactors will first be experimented with butane under varying reaction types. After which key components of JP-8 will then be tested, requiring the addition of a vaporizer. These experiments will move us closer to the final goal of reforming JP-8 to provided portable power on the battlefield. The results of the experiments discussed above will be presented at the conference in detail.

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References

1. G. Petitpas, J.-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, L. Fulcheri, "A comparative study of non-thermal plasma assisted reforming technologies," *International Journal of Hydrogen Energy*, **32**, 2848-2867 (2007).
2. T. Paulmier, L. Fulcheri, "Use of non-thermal plasma for hydrocarbon reforming," *Chem. Eng. J.*, **106**, 59-71, (2005).
3. M.V. Mundschau, C. G. Burk, D. A. Gribble Jr., "Diesel fuel reforming using catalytic membrane reactors," *Catalysis Today*, **136**, 190–205, (2008).
4. Lt. Col. John LaTulip, "Lessons Learned from Operation Iraqi Freedom," *Tri-Services Power Expo*, Norfolk, VA, (2003).
5. D. R. Cohn, L. Bromberg, K. Hadidi, "Onboard Plasmatron Hydrogen Production For Improved Vehicles," *MIT Plasma Science and Fusion Center*, (2006).
6. Wikipedia contributors, "Plasma (physics)," *Wikipedia, The Free Encyclopedia*, (2008). Available at:
[http://en.wikipedia.org/w/index.php?title=Plasma_\(physics\)&oldid=233794520](http://en.wikipedia.org/w/index.php?title=Plasma_(physics)&oldid=233794520).
7. Wikipedia contributors, "Fusion Energy," *Wikipedia, The Free Encyclopedia*, (2008). Available at:
http://en.wikipedia.org/w/index.php?title=Fusion_power&oldid=233899672.
8. H. Scott Fogler, "Elements of Chemical Reaction Engineering 3rd Edition", *Prentice Hall PTR*, (1999).
9. Wikipedia contributors, "Activation Energy," *Wikipedia, The Free Encyclopedia*, (2008). Available at:
http://en.wikipedia.org/w/index.php?title=Activation_energy&oldid=231344369.
10. B. Cannella "Refining and Distillate Fuel Trends," 4th *DoD Logistics Fuel Reforming Conference*, October 22-23, Philadelphia, PA, (2003).
11. D. J. Moon, J. W. Ryu, K. S. Yoo, D. J. Sung, S. D. Lee, "Development of iso-octane fuel processor system for fuel cell applications," *Catalyst Today*, **136**, 222–227, (2008).
12. K. Becker, Final Report, "Compact Plasma Reactor for Ship Service Fuel Cell System," *Office of Naval Research Ship Service Fuel Cell Program*, pg 234, (2004).
13. D. Dietz, H. Ghezal-Ayagh, J. Hunt, A. Belkind, K. Becker, and A. Nickens, "Plasma Treatment of a Heated Diesel/Steam Mixture for Use in Ship Services Fuel Cell Systems", *Proc. 31st IEEE ICOPS*, Baltimore, MD, pg.412, (2004).
14. R. Foest, M. Schmidt, K. Becker, "Microplasmas, an emerging field of low-temperature plasma science and technology," *International Journal of Mass Spectrometry*, **248**, 87-102, (2006).
15. X. Ouyang, L. Bednarova, P. Ho, and R.S. Besser, "Preferential Oxidation of Carbon Monoxide in a Thin-Film Catalytic Microreactor: Advantages and Limitations," *AIChE J.*, **51** (6), 1758-1772, (2005).
16. J. Reece Roth, "Industrial Plasma Engineering", *Institute of Physics Publishing, Bristol and Philadelphia*, (1995).