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CURRENT, NON-THERMAL PLASMA BOOSTED
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HYDROGEN MANUFACTURING USING LOW CURRENT, NON-THERMAL PLASMA BOOSTED FUEL CONVERTERS

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Introduction

Hydrogen-rich gas can be efficiently produced in compact plasma boosted reformers by conversion of a variety of hydrocarbon fuels including natural gas and diesel. A novel type of plasma reformers, using a low current, high voltage non-thermal plasmatron which we have recently developed, has been investigated. Use of a low current nonthermal plasmatron greatly reduces the specific electrical energy consumption and the electrode wear relative to thermal arc plasma reformers. The performance of the novel plasmatron configuration is described in this paper.

Plasma technology has potential advantages over conventional means of manufacturing hydrogen. The shortcomings of the conventional reformers include the need of large scale plants, cost and deterioration of catalysts; size and weight requirements; limitations on rapid response; and limitations on reformation of heavy hydrocarbons.

The main disadvantage of plasma reforming is the dependence on electrical energy. The new low current plasmatron described in this paper makes it possible to overcome this problem and drastically decrease energy consumption.

The combination of new low current plasma boosted reformer with rapid start-up metallic catalyst and simple counterflow heat exchanger make possible to develop a conceptual design for compact highly efficient multi-fuel plasma processor for fuel cell power generation and other applications.

Plasma boosted reforming may allow economically attractive operation at small hydrogen production levels. The low current plasmatron fuel converter technology is being developed for hydrogen manufacturing for a variety of stationary applications including distributed, low pollution electricity generation from fuel cells; hydrogen-refueling gas stations for fuel cell powered cars; and decentralized hydrogen generation for industrial processes. It is also being developed for potential use with internal combustion engine vehicles.

In this paper, recent results of plasma boosted reformation of methane and diesel are discussed. The composition of the reformat for varying air-steam-fuel ratios, varying throughput and varying electrical power will be reported.

Experimental setup

Reagents Hydrocarbon fuels and air. The air used for the plasmatron fuel converter was provided from the compressed air in the building. No special handling or preparation of the air was made.

The methane used was provided from bottled gas, with a purity of 99.99%. The liquid fuels used were obtained from a local gasoline station, and no characterization of the fuel was performed.

Both gas phase reactions as well as catalytic reactions were studied for air/fuel and air/fuel/water vapor mixtures injection. In the heterogeneous experiments, nickel based catalyst on alumina support was used. The catalyst (United Catalyst C-11) came in rings, and best results were obtained with crushed catalysts to 5 mm average size.

Potable water was the source of the steam.

Characterization methods. The gas analysis was performed using a HP M200D GC, with two columns and with two thermal conductivity detectors. Calibration gases were provided by Matheson Gas.

Plasmatron fuel converter. Plasmatrons are electrical devices that take advantage of the finite conductivity of gases at very elevated temperatures. At these temperatures, the gas is partially ionized and electrically conducting. Plasmatron fuel converters provide electrical discharges in flowing gases of hydrocarbon fuels and air (and/or other oxidants). The resulting generation of reactive species in the flowing gases along with increased mixing accelerates reformation of hydrocarbon fuels into hydrogen rich gas.

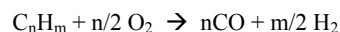
Plasmatron fuel converters may also be utilized for increasing the gas stream enthalpy, further accelerating the reaction rates. These conditions facilitate the reforming of a wide range of hydrocarbon fuels into hydrogen-rich gas. The high temperatures can be used for reforming a wide range of hydrocarbon fuels into hydrogen rich gas without the use of a catalyst. With the use of a catalyst, as in the case of plasma catalysis [1] the plasma is an excellent fuel preprocessor, since it can vaporize even heavy hydrocarbons and thus could provide a source of hydrogen that can be used with many fuels.

The plasmatron would be used to boost the temperature and kinetic reactions in a reformer, resulting in hydrogen-rich gas production throughout a wide range of operation, from partial oxidation to steam reforming. The boosting of the conversion process would occur as a result of the creation of a small region with very high electron temperatures (3000-10000 K) where radicals are produced and as a result of increasing the average temperature in an extended region.

The additional heating provided by the plasmatron would serve to ensure a sufficiently high number of chemically reactive species, ionization states, and temperatures for the partial oxidation or other reforming reaction to occur with negligible soot production and a high conversion of hydrocarbon fuel into hydrogen rich gas. The effective conversion of hydrocarbon fuel is aided by both the high peak temperature in the plasma and the high turbulence created by the plasma. These features should facilitate the use of plasmatron devices for reforming heavier hydrocarbons including biofuels and waste oils.

By increasing the reaction rates, plasmatron fuel converters can reduce size requirements for effective reforming, relax or eliminate catalyst requirements, increase speed of response and increase fuel flexibility. A wide range of fuels can be converted to hydrogen rich gas. The boost provided by the plasma can facilitate partial oxidation reactions with negligible soot production and efficient conversion of hydrocarbon fuel into hydrogen-rich gas. Plasmatron fuel converters can alleviate problems associated with catalytic reformation, such as response time limitations, sensitivity to fuel composition, poisoning, soot formation and a narrow operational temperature range.

Under ideal stoichiometric partial oxidation conditions, the partial oxidation reaction is



In this case there is just enough oxygen around to convert all the carbon in the fuel into CO. The partial oxidation reaction is exothermic. In the case of liquids fuels (gasoline, diesel), approximately 15% of the heating value of the fuel is released in the partial oxidation reaction.

The plasmatron fuel converter provides continuous ignition at the entrance of the fuel, and helps in the gasification of the fuel. By generating radicals throughout the volume, limitations due to slow flame propagation are alleviated, facilitating partial oxidation reactions over the whole reactor volume, increasing conversion efficiency and reducing soot formation.

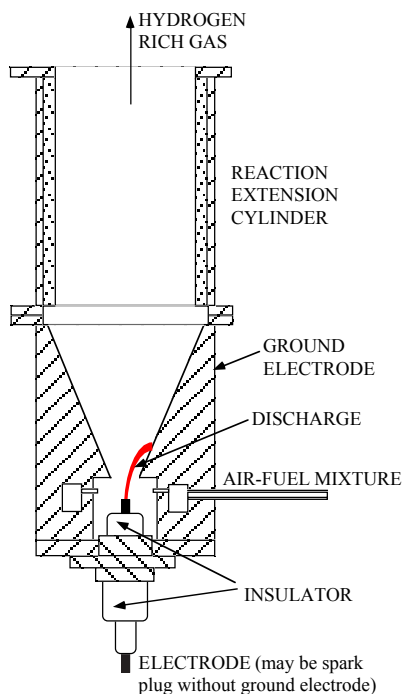


Figure 1. A low current plasmatron fuel converter.

Table 1.

Parameters of low current compact plasmatron fuel converter

Power	50-300 W
Current	15-120 mA
H ₂ flow rate	30-50 liters/min
Height	25 cm
Volume	2 liters
Weight	3 kg

The plasmatron employs a discharge mode with non-equilibrium features allowing operation at much reduced plasma current relative to compact arc plasmatron fuel reformers previously developed at MIT [1,2]. The discharge is a nonthermal plasma, with electrons at much higher temperature than the ions and neutrals, which are at near room temperature. This plasma generates relatively low levels of plasma heating. Figure 1 shows a diagram of a low current plasmatron reformer. Air and fuel are continuously injected in a plasma region provided by a discharge established across an electrode gap. The device operates at atmospheric pressure, with air as the plasma forming gas. When operating DC, the cathode can be a heavy duty spark plug. The ground electrode of the spark plug would have been removed. The anode can be a steel or copper cylinder.

Neither electrode is water cooled. A variety of electrode and injection geometries are possible.

Table I shows the parameters of a first generation fuel converter using a low current compact plasmatron. Typical electrical power levels are a few hundred Watts, on the order of 1-2% of the heating value power of the fuel that is processed by the plasmatron fuel converter. This electrical power loss results in a drain of 3 to 5% of the chemical power of the fuel in order to produce the electricity. Most of the heating is provided by the exothermicity of the partial oxidation reaction. The partial oxidation heating can be increased by operating with increased oxygen to carbon ratio (i.e., combusting a fraction of the reformat). This additional heating is specially important during the start-up phase of the fuel converter. However, this additional heating decreases the hydrogen yield.

The plasma source is followed by a reaction extension cylinder. For tests with the addition of water, a simple heat exchanger was added downstream from the reaction extension cylinder, both to cool the reformat and to produce steam.

Second generation low current plasmatron fuel converters have recently been tested. In these compact devices both electrodes have relatively large area, in contrast to the first generation device shown in Figure 1. They produce a discharge over a relatively large volume and have been operated at significantly higher powers than the first generation low current plasmatrons. This type of low current device has been used to convert natural gas, gasoline and diesel fuel into hydrogen rich gas. There was minimal evidence of soot production in the processing of diesel fuel, even after extended operation. Typical power conversion efficiencies in the partial oxidation mode were 60-85% (ratio of heating value of the product gas to heating value of the fuel). Diesel fuel streams with chemical power levels of 5 to 20 kW have been processed into hydrogen rich gas.

Results and Discussion

The use of the low current plasmatron has allowed substantial reductions in the electrical power requirements for the plasmatron. Figure 2 shows the hydrogen yield, defined as the fraction of the hydrogen in the fuel that is released as hydrogen, as a function of the specific energy consumption, defined as the ratio between the electrical consumption in the plasmatron to the heating value of the hydrogen generated by the reforming. Results are shown for a low current nonthermal plasmatron fuel converter (□new plasmatron□), and an arc plasmatron fuel converter (□oldplasmatron□). Figure 2 is for methane. Even better results have been obtained for diesel, as shown in Figure 3. For methane, for both the previously reported thermal plasma reformer, and for the nonthermal plasmatron. This results include partial water shifting of the CO, as will be described below.

These results indicate a better than 70% conversion efficiency, with an electrical energy input of less than 3% of the heating value of the fuel. They also demonstrate high efficiency water shifting in a compact unit. They summarize results from a large number of experiments, that will be described in more detail below.

Synthesis gas production. For certain application, synthesis gas is the desired product from the reformer. In this case, little or no addition of water/steam is required.

Table 2 shows reforming results for several cases, using the second generation plasmatron fuel converters, at steady state conditions (after about 1 to 2 minutes). Several types of reaction extension cylinders were used with either no catalyst or a catalyst in the reaction extension cylinder. The effect of the presence of water was also studied. The purpose of the water addition is to convert, via

a water-shift reaction, a large fraction of the CO generated in the plasmatron fuel converter into additional hydrogen, for those applications where hydrogen is much more preferred than CO. Hydrogen yields higher than 100% (H₂ in product gas divided by hydrogen in fuel) can be achieved with the use of a catalyst and water shifting. Power conversion efficiencies of close to 90% have also been obtained under certain conditions. For onboard applications, it is difficult to provide the required water onboard vehicles, and this issues could be a major deterrent to the use of the water shift reaction for onboard applications for internal combustion engines.

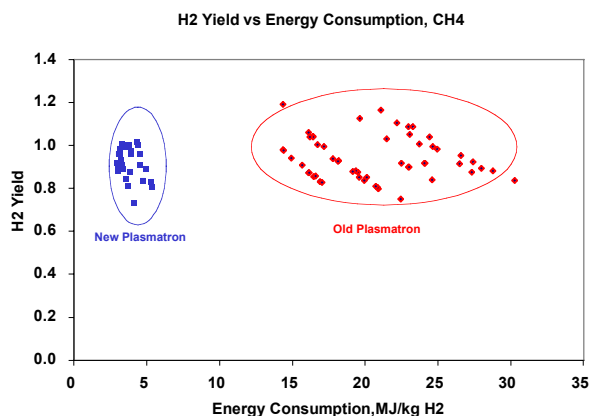


Figure 2. Hydrogen yield for methane as function of the specific energy consumption, for both the thermal plasmatron (Old Plasmatron) and the nonthermal plasmatron (New Plasmatron).

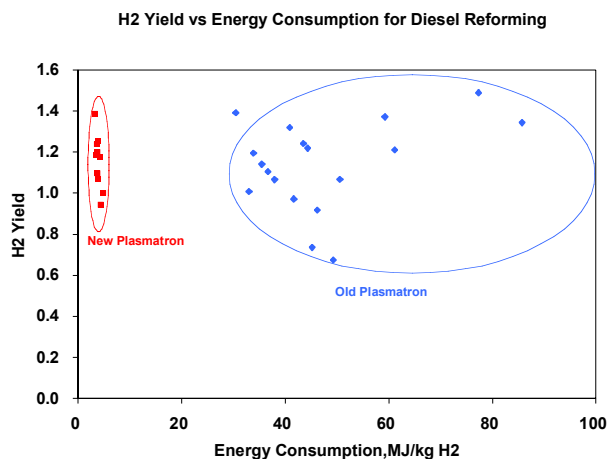


Figure 3. Same as Figure 2., but for diesel fuel.

Typical second generation low current plasmatron fuel converter parameters were a power levels of 300W to 600W, oxygen/carbon ratios (O/C) of 1.2-1.5, and fuel rates of 0.3-0.5 g/s (corresponding to about 10-20 kW of fuel power).

The composition of the hydrogen rich gas for the cases in Table 2 are shown in Table 3. High concentrations of hydrogen and CO are obtained. It appears to be possible to operate the low current plasmatron fuel converter in modes with minimal production of soot.

Startup transients. The startup yield of the plasmatron fuel converter has been investigated with both diesel and gasoline fuel [3]. The composition of the hydrogen rich gas was studied as a function

of time. Hydrogen yields as high as 30% are instantaneously obtained (in times less than 3 seconds), increasing to as high as 80% after 90 s. The power conversion efficiency is about 30% at startup, increasing to 70-80% after the reactor has warmed up. Similar performance has been obtained in both fuels.

Previously, diesel fuel has been successfully reformed at O/C ~ 1 using a compact plasmatron reformer that employs a DC arc plasmas [2]. However, arc plasmatron reforming utilizes substantially higher electrical powers and currents.

Table 2.

Second generation low current plasmatron fuel converter
Cases for different catalysts, O/C ratios and presence/absence of additional water, with diesel fuel

	Electrical Power kW	O/C	H ₂ O/C	Fuel g/s	Fuel Power kW	Hydrogen yield	Energy Consumptior MJ/kg	Energy Convers
Empty reactor	0.27	1.3	0.0	0.26	11.1	0.64	13.2	56
Ceramic catalyst	0.19	1.5	0.0	0.48	20.6	0.75	4.3	64
Honeycomb catalyst	0.23	1.3	0.0	0.31	13.3	1.00	6.1	81
Honeycomb catalyst water (2 excess)	0.15	1.2	1.8	0.31	13.1	1.22	3.3	87
Honeycomb catalyst water (4 excess)	0.11	1.4	4.0	0.22	9.5	1.30	3.2	72

Table 3.

Gas composition for cases in Table 2.

	H ₂ vol.%	CO vol.%	CO ₂ vol.%	N ₂ vol.%	CH ₄ vol.%	C ₂ H ₄ vol.%
Empty reactor						
Ceramic catalyst	14	16	4.7	64	0.7	0.1
Honeycomb catalyst	14	17	4.7	64	0.2	0.0
Honeycomb catalyst water (2 excess)	19	21	3.3	57	0.3	0.0
Honeycomb catalyst water (4 excess)	23	11	10.9	56	0.4	0.0

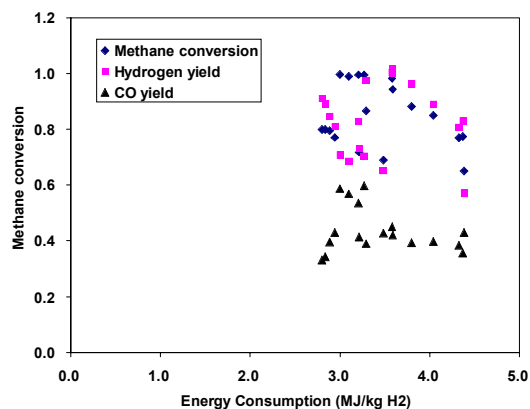


Figure 4. Power efficiency of low current plasmatron fuel converter for methane as a function of energy consumption, for varying OC ratios and water to carbon ratio.

Hydrogen generation from methane. For hydrogen generation (with low content of CO), natural gas plasma reforming at atmospheric pressure was carried out with a metallic catalyst. The catalyst support used in these experiments was obtained from EMITEC with Pt/Rh coating (proprietary catalysts coating developed

by Engelhardt Corp.). The mixture of air, natural and steam was injected into the plasma discharge. The mixture started to react in the region following the discharge in a homogeneous mode, prior to reaching the catalyst. High methane conversion can be found in this mode of operation, as shown in Figure 4. The estimated heating value of the reformat has been found to be as high as 80-90% of the heating value of the fuel.

Plasma usage make it possible to combine in one reactor 2 stages- partial oxidation and crude water shift reaction producing highly enriched synthesis gas (vol%: H₂-35%; N₂-47%; CO-3%; CO₂-13%). The composition of the reformat is given in Table 4 for a range of parameters.

Table 4

Preliminary results of plasma catalytic reforming of methane

Power input (kW)	0.21	0.21
Flow rate (g/s)	0.22	0.191
O/C ratio	1.46	1.72
H ₂ O/C ratio	4.1	3.37
Reformat composition		
H ₂ vol%	34.5	31.6
CO vol%	3.2	7.1
CO ₂ vol%	13	9.7
N ₂ vol%	47.2	51.2
CH ₄ vol%	1.9	0.3
CH ₄ conversion	89%	98%
CH ₄ to H ₂	100%	67%
CH ₄ to CO	19%	45%

Hydrogen Yield vs 2O₂/mCmHn ratio for different H₂O excess

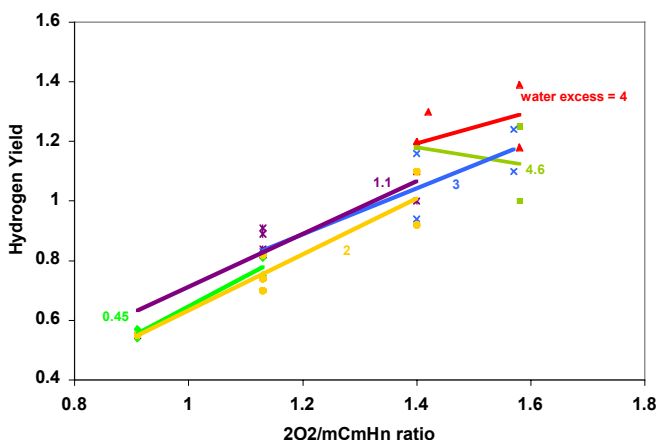


Figure 5. Hydrogen yield as a function of the oxygen to carbon ratio, for several steam to carbon ratios.

Electrical energy consumption in these preliminary experiments with the low current plasmatron was very low - 2-3 MJ/kgH₂ even without the use of heat exchanger. This is an order of magnitude less than our previous results with low voltage high current arc plasmatron.

The energy conversion efficiency, defined as the ratio between the heating value of the reformat and the heating value of the initial

fuel, is on the order of 80%. This occurs without the use of heat exchangers and improved process parameters. Further improvements in the case of methane is expected in the near future. It is estimated by extending the diesel work to methane, and with improved process parameters, the energy efficiency of the case of natural gas could be as high as 90-95%.

If should be noted that the water shift reaction is incomplete. This is because of the lack of a low temperature water shift.

Hydrogen generation from diesel. Preliminary reforming experiments with the plasmatron fuel converter have also been carried out with diesel. In this case, although the diesel conversion is high, the efficiency of the water shifting section of the reactor is not as efficient as in the case with methane. The CO concentration at the output of the reformer is on the order of 6%, due in part to the high gas temperature (less low temperature water shift). In the near future, experiments with diesel will be carried out with better temperature and space velocities in the water shifting reactor.

The hydrogen yield in the plasmatron fuel reformer is shown in Figure 5 as a function of the oxygen to carbon ratio, for various steam to carbon ratios. In this case, the maximum yield (as defined above) is on the order of 2. The yields in Figure 5 are substantially lower because of the incomplete water-shift conversion of CO into hydrogen.

Summary. In summary, experimental studies of low current nonthermal plasmatron fuel converter operation indicate that this approach may provide a more compact, robust, responsive and lower cost means of converting a variety of hydrocarbon fuels into syngas or hydrogen.

Acknowledgments

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