PSFC/JA-99-4

Plasma Reforming of Diesel Fuel

L. Bromberg, A. Rabinovich,
N. Alexeev,and D.R. Cohn

March 1999

Plasma Science and Fusion Center
Massachusetts Institute of Technology
Cambridge, MA 02139

0

Abstract

The use of a plasma reformer for the generation of hydrogen rich gas from diesel fuel has been investigated. A system that is normally used for investigating natural gas reforming has been modified in order to investigate the reforming of heavy liquid fuels. The composition of the reformate has been investigated as a function of the composition of the reagents. The use of a one-step reformer/water shifter was studied. Good reforming, with no noticeable soot production, was obtained. The specific energy consumption was equal to that previously obtained with methane reforming, with much reduced concentration of methane in the reformate.

1. Introduction.

Thermal plasma technology can be efficiently used in the production of hydrogen and hydrogen-rich gases from methane and a variety of fuels [1-3]. The thermal plasma is a highly energetic state of matter that is characterized by extremely high temperatures (several thousand degrees Celsius) and high degree of dissociation and substantial degree of ionization. The high temperatures accelerate the reactions involved in the reforming process. Hydrogen-rich gas (40% H_2, 17% CO_2 and 33% N_2, for partial oxidation/water shifting) can be efficiently made in compact plasma reformers from natural gas.

Plasmatrons are electrical heating devices that take advantage of the finite conductivity of gases at very elevated temperatures. At these temperatures, the gas is partially ionized. Plasmatrons provide highly controllable electrical heating of this ionized 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. Thus it would be possible to eliminate problems associated with catalysts , such as narrow operating temperatures, sensitivity to fuel composition, poisoning, and slow response times.

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 very high temperature region (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.

The plasma conditions (high temperatures and a high degree of dissociation and substantial degree of ionization) can be used to accelerate thermodynamically favorable chemical reactions without a catalyst or provide the energy required for endothermic reforming processes. [3] Plasma reformers can provide a number of advantages:

- compactness and low weight (due to high power density)
- high conversion efficiencies
- minimal cost (simple metallic or carbon electrodes and simple power supplies)
- fast response time (fraction of a second)
- operation with a broad range of fuels, including heavy hydrocarbons (crude) and with "dirty" hydrocarbons (high sulfur diesel).

The technology could be used to manufacture hydrogen for a variety of stationary applications e.g., distributed, low pollution electricity generation from fuel cells [1].The ability to rapidly vary the plasmatron parameters (energy input, flow rate, product gas composition, etc) makes this technology very attractive for applications with dynamic demands of hydrogen rich gas.

In the past, plasmatron systems have been used in the reforming of natural gas. [3] In the case of natural gas, for partial oxidation/water shifting, it was determined that the specific energy consumption in the plasma reforming processes is 16 MJ/kg H_2 with high conversion efficiencies. A one stage system has been demonstrated for hydrogen production with low CO content (~1.5%) with power densities of ~30 kW (H_2 HHV)/liter of reactor, or ~10 m^3/hr H_2 per liter of reactor. Power density should further increase with increased power and improved design.

This paper extends the previous work in natural gas in plasma reforming experiments to the conversion of diesel fuels using heterogeneous processes. Section 2 describes the experimental setup. Section 3 describes the results for a given set of plasmatron parameters as a function of the reagent composition. Finally, Section 4 described the conclusions and directions for future work.

2. Description of the Setup

In this section, the experimental facility, as well as the methods and reagents used, are described.

A schematic diagram of a plasmatron is shown in Figure 1. The arc is generated between the water-cooled cathode with a hafnium tip, and a water-cooled tubular anode. The gas to the plasmatron has a large vorticity in order to spin the arc, centering the cathode arc root in the hafnium tip, and rotating the anode spot.
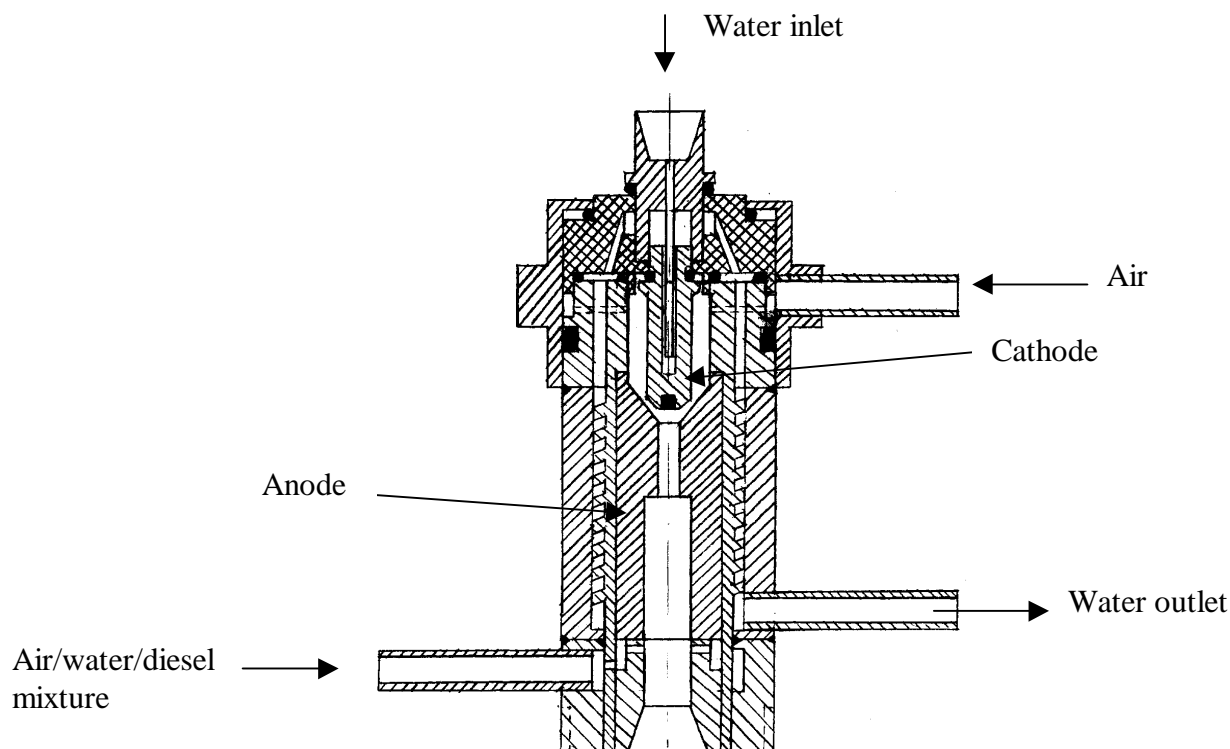

Figure 1. Schematic diagram of the plasmatron.

The diesel was injected downstream from the arc, as shown in Figure 1.

Both gas phase reactions as well as catalytic reactions were studied for air and air/water vapor mixtures injection into an air plasma. 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.

Drinking water was the source of the steam. 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. The diesel fuel was acquired from a local gas station, and was not characterized. The sulfur content of the diesel was not measured, but was probably around 500 ppm.

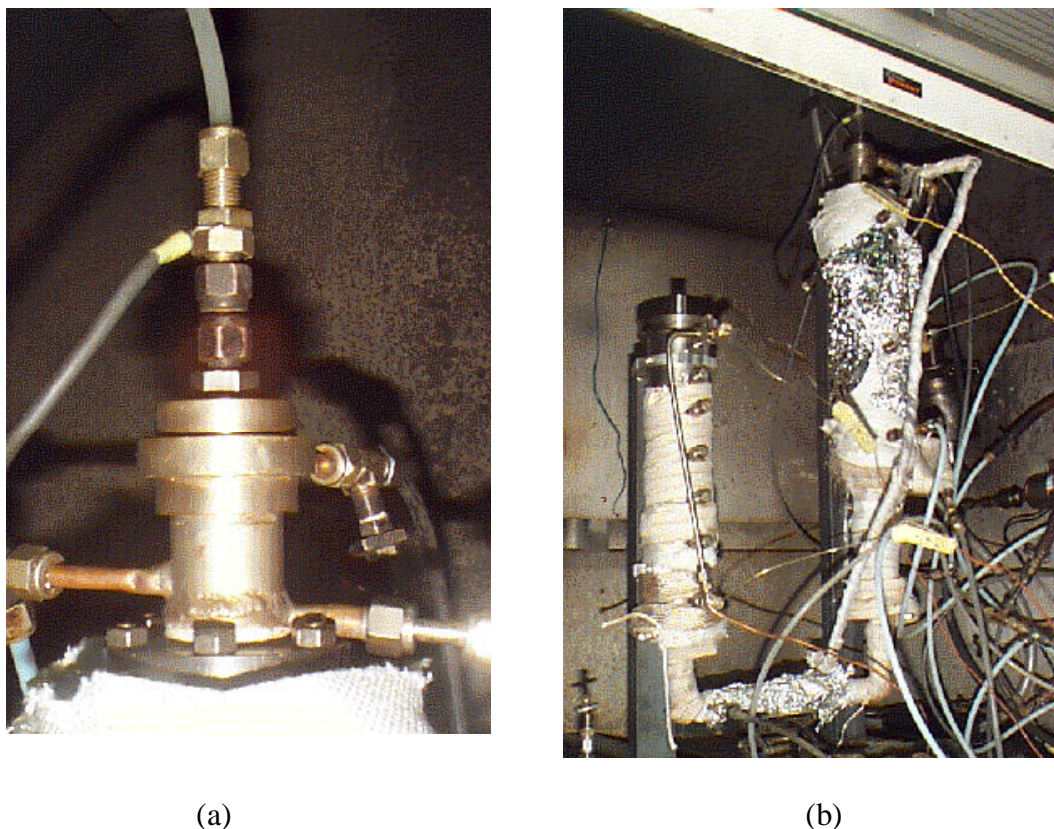(a)   (b)

Figure 2. Photograph of plasmatron used in experiment. Photograph of the advanced reactor setup.

A picture of the plasmatron that was used in the experiments is shown in Figure 2(a). The arc parameters were 18A and about 120 V for the experiments described in this paper. Due to limitations in time, the power was not varied.

Figure 3 shows an schematic of the plasmatron and the catalytic reactor. The catalytic reactor consists of 3 sections: the first one is made of 3 mm (1/8 in) steel walls, a double wall section, and an air-heat exchanger.

The reactor has an internal diameter of 4 cm (1.5 in) and is insulated with an insulating coating of Saureisen, 0.5" thick. In addition, the outside of the reactor is also insulated with thermal insulation blanket (Zircon). The catalyst was placed in the first two sections of the reactor, filling all the available space. Due to resource limitation the temperature of the catalyst in the reactor was not measured. The temperatures of the steam and preheated air were measured.

4

The diesel, air and water prior to injection into the system were preheated in different methods in the experiments, as described in the next section..

In the experiments described in this paper, the diesel flow was 0.31 –0.4 g/s. The air flow rate was varied around partial oxidation conditions, and the water to carbon ratio was varied from 1.16-2.6.
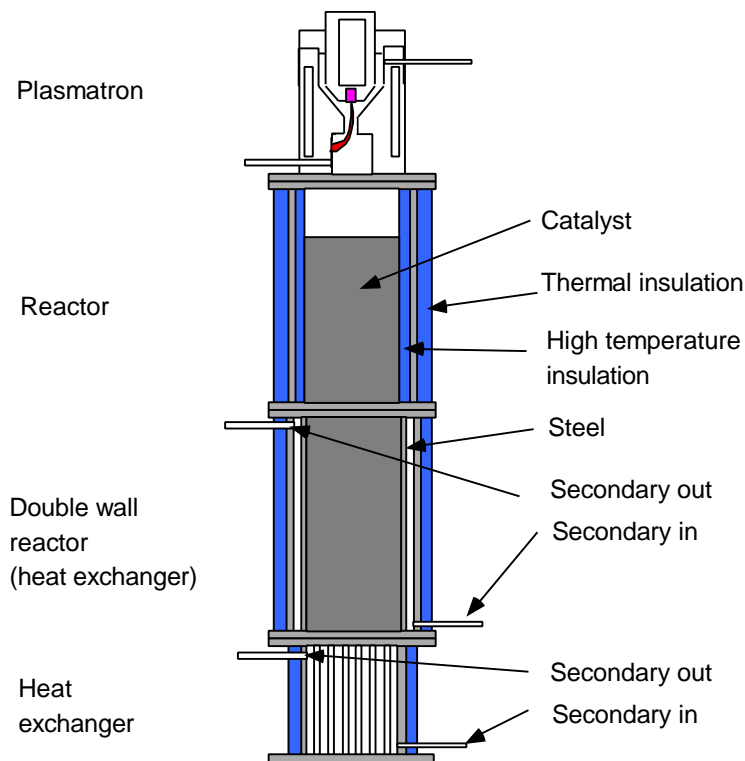
Plasmatron

Reactor

Catalyst

Thermal insulation

High temperature insulation

Steel

Secondary out

Secondary in

Double wall reactor (heat exchanger)

Heat exchanger

Secondary out

Secondary in

Figure 3. Schematic diagram of plasmatron, reactor, double wall reactor and heat exchanger

3.   Experimental results.

Three sets of experiments were carried out, in accordance with the process equipment design. The main difference in the experimental setup of the equipment design was in the preheating schemes.

First process setup

The first set of experiments was carried out without diesel preheating. The air was preheated in the heat exchanger. The water and preheated air were subsequently introduced in the double wall section. The preheated air and water, and the diesel, were injected into the plasmatron. The water to carbon ratio in these experiments varied from 1.6-2.6, with a diesel flow rate of 0.31 g/s. The power input was held near constant in these experiments.
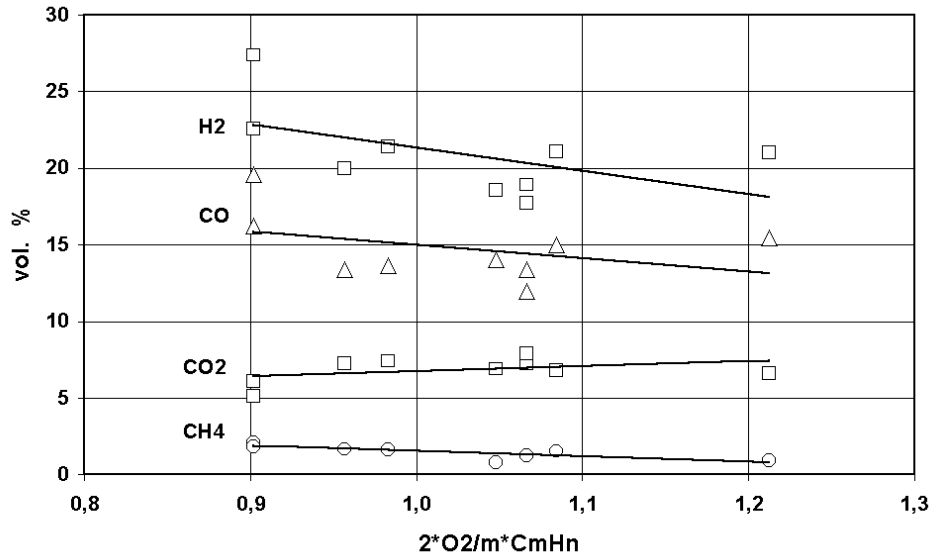
Fig. 4. Composition of the reformate for the case of no preheat of diesel fuel.

The composition of the reformate in this case is shown in Figure 4. The oxygen to carbon ratio was varied. Partial oxidation corresponds to 1 in the ordinate scale. This results indicate that very little methane was generated, less than about 2 %. The concentration of CO was lower than that of hydrogen, indicating that some steam reforming or water-shifting has occurred. For partial oxidation with no water shifting, the ideal composition of the reformate is 25% H_2, 25% CO and 50% N_2 (assuming CH_2 as the carbon/hydrogen ratio in the fuel).
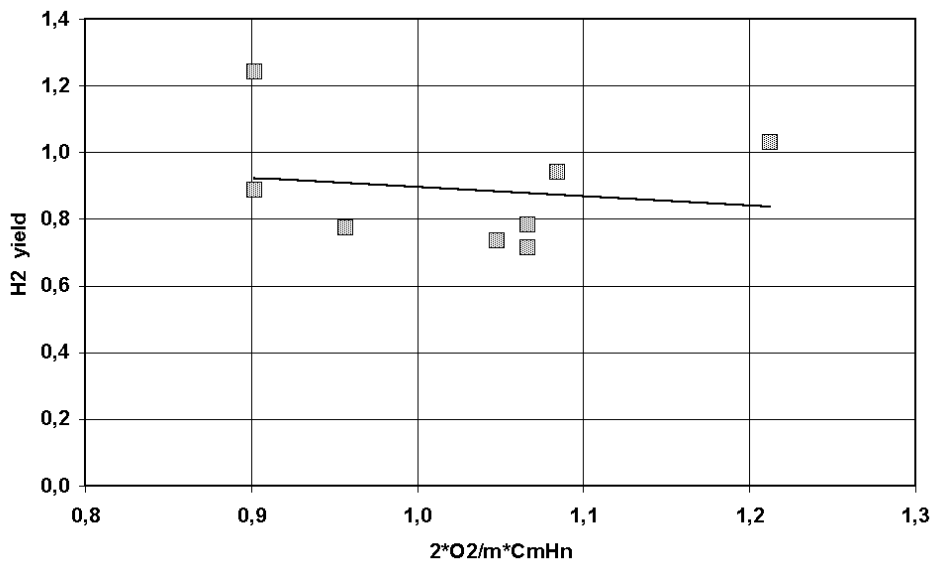

Figure 5. Hydrogen yield in diesel reforming. No preheating of the diesel.

The corresponding hydrogen yield is shown in Figure 5. The hydrogen yield varies between 0.8 and 1.2. The hydrogen yield has a small minimum under conditions of partial oxidation, increasing to both directions of pyrolysis and combustion.

6

It should be noted that the ideal hydrogen yield is 1.9, if all the CO is water shifted into H_2. However, as can be seen in Figure 4, only about 1.3 of the CO was water shifted in our experimental setup.
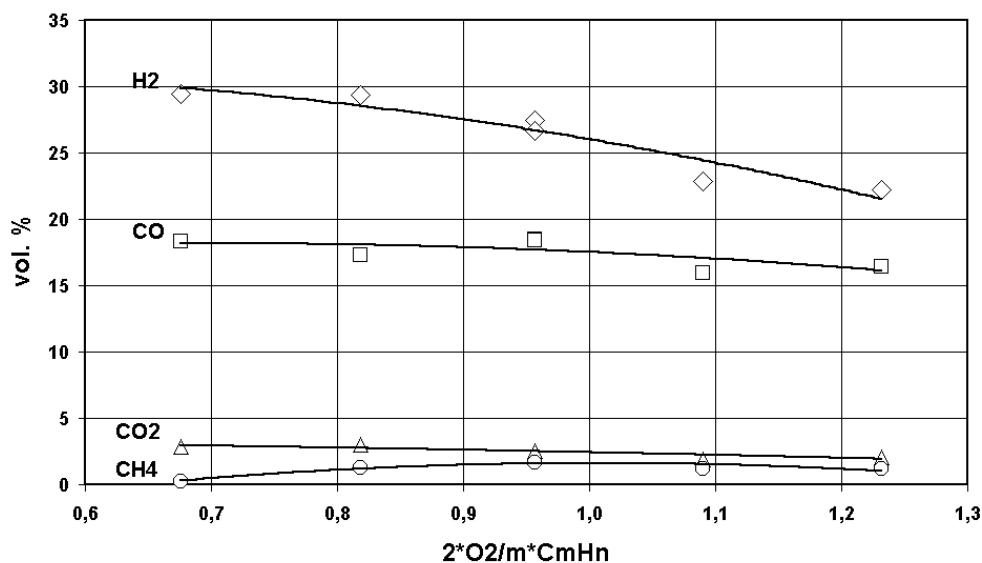

Figure 6. Composition of the reformate with air, diesel and water preheating

Second process setup

In the second set of experiments, air was heated in heat exchanger, with the water and diesel evaporation (preheating) in reactor with double walls. In this set of experiments, the diesel flow rate was held constant to about 0.39 g/s, and the water to carbon ratio was varied between 1.4 and 1.8.
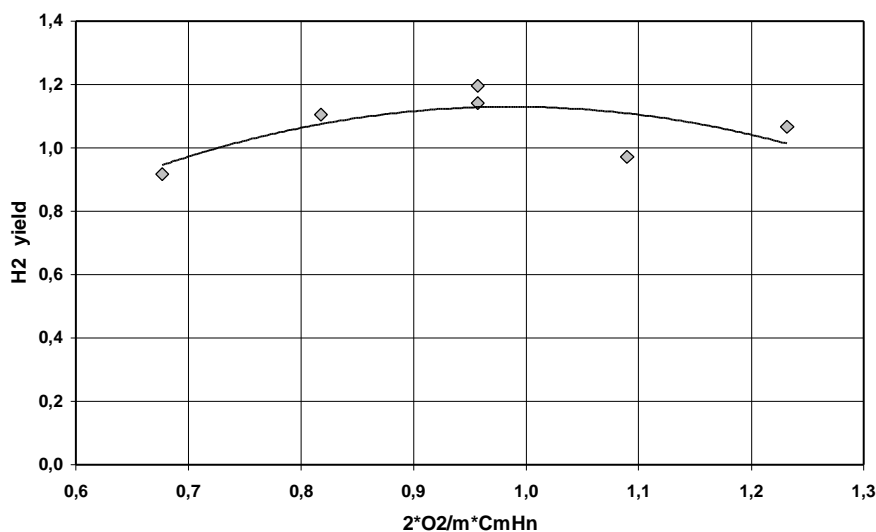

Figure 7. Hydrogen yield in the case of air, water and diesel fuel preheating.

Figure 6 shows the composition of the reformate, while figure 7 shows the hydrogen yield. In this case, the maximum hydrogen composition occurs at condition on the pyrolysis side of partial oxidation. Due

to the fact that the exact fuel composition is unknown, the real stoichiometric partial oxidation conditions could be different from what is shown as 1 in figures 6 and 7. However, the CO is very little converted in the system, since the CO_2 concentration are very small, at most 3% and the CO concentrations are around 20 %. Towards the pyrolysis side, the methane yield was also very small, increasing slightly towards partial oxidation conditions.

Third process setup

In the last set of experiments, water was preheated in the reactor with double walls, without air preheating. The diesel fuel was preheated electrically. The diesel flow rates were comparable to those in the previous set of experiments (0.39 g/s), and the water to carbon ratio was 1.22-1.64.
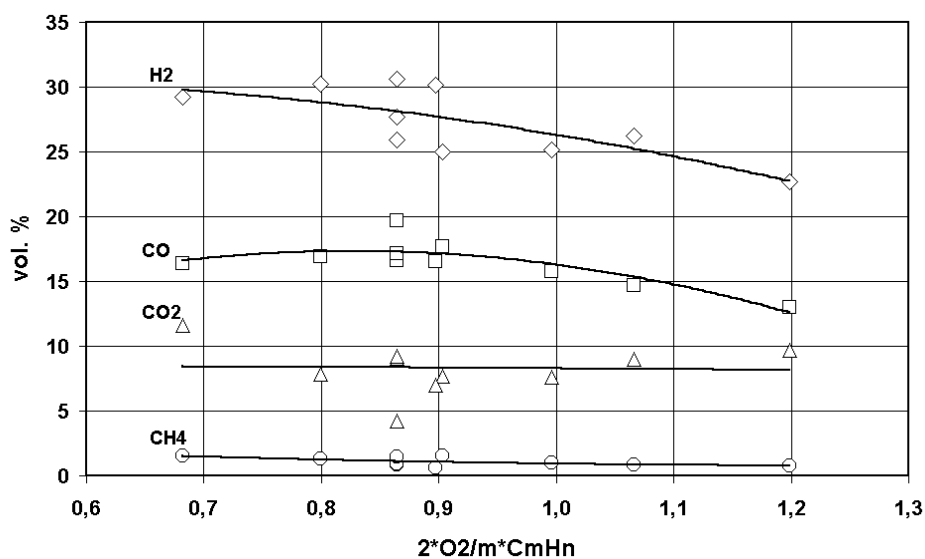

Figure 8. Composition of reformate in the case of no air preheating.

Figure 8 shows the composition of the reformate. As in case 2, the maximum hydrogen concentration occurs on the pyrolysis side of partial oxidation. There is still little conversion of the CO through water-shift reaction. The corresponding hydrogen yield is shown in Figure 9. This case shows the largest hydrogen yield from all the cases studied, about 1.4 (from a maximum possible yield of 1.9). The methane concentration at the maximum hydrogen yield is also the smallest for the three cases investigated.

Also shown in Figure 9 are the results for a 50% greater fuel flow rate (with corresponding increases in the air and the water flows). The results are lower for the cases investigated (towards pyrolysis from partial oxidation). If the results can be extrapolated, it seems likely, though that at conditions of partial oxidation the hydrogen yield is not going to be much lower than in the case of lower throughputs.

4. Discussion and directions of future work.

Preliminary results of using a plasma reformer for conversion of diesel fuels have been presented. Although preliminary, several things have been well established:

- There is no creation of soot, even in conditions that are on the pyrolysis side of partial oxidation.
- There are no higher hydrocarbons in the reformate than methane.
- Methane yields are low, less than about 3% under most conditions.
- The highest hydrogen field has been achieved under condition where diesel fuel was electrically preheated and partially vaporized.

The composition of the reformate with the highest hydrogen yield (1.4) is (vol%): 28%-30% H_2, 14%-20% CO, 4.2%-7.6% CO_2, 0.6%-1.5% CH4, and the balance is N_2. The ethane concentration was measured to be less than 0.1%. The specific energy consumption is 29-32 MJ/kg H_2.
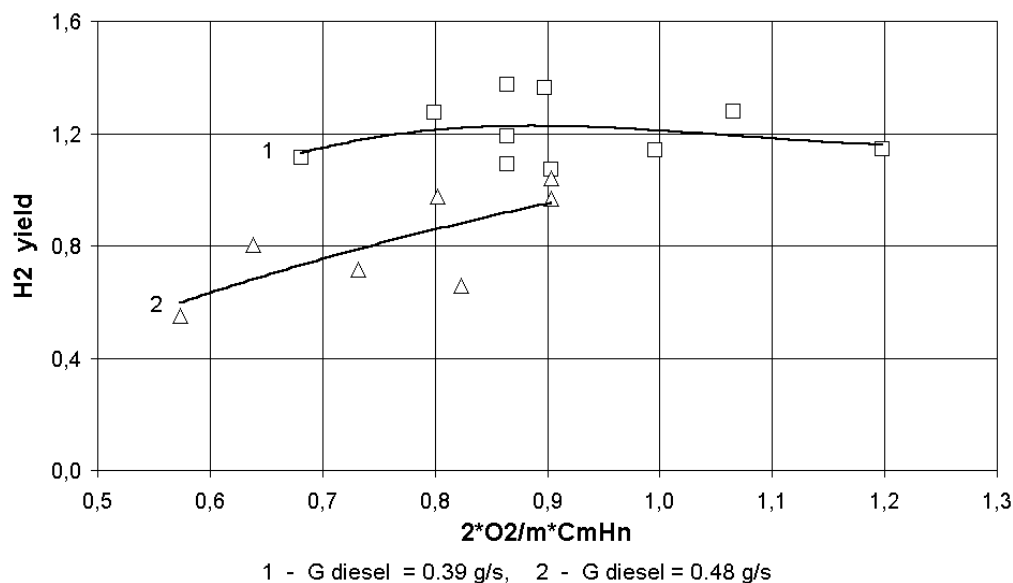

1 - G diesel = 0.39 g/s, 2 - G diesel = 0.48 g/s

Figure 9. Hydrogen yield for the case of water/air preheat, no air preheating

Table 1 shows a comparison between the plasma catalytic reforming of methane [3] and diesel fuel.

Table 1. Comparison of plasma catalytic reforming of diesel and methane.

	Methane	Diesel
Total H2+CO content (vol%)	42-49	44-50
CH4 content (vol %)	5.9-6.4	0.6-1.5
Energy consumption (MJ/m^3 of H2 and CO)	1.4-1.7	1.5-1.7

The energy consumption of H2 + CO mixture is practical equal to both types of fuel, but the remaining methane concentration in the reformate gas is much lower for the diesel fuel. It shows higher conversion efficiencies for diesel reforming. Produced mixture of H_2 + CO could be readily reformed to H2 + CO2 without any additional energy consumption in the second stage of the process via a conventional water-shift reaction.

The single step reforming/water shifting results that were obtained previously with methane, could not be reproduced with diesel fuel. Several setups were used to try to improve this condition, mainly affecting the process equipment (heat exchanger, vaporization of water/diesel, etc). In the end, we built

a advanced reactor (see Figure 2b), with multiple temperature monitoring along the reactor (6 thermocouples along the axis), and connected it to a second reactor, where water shifting could be tried if the first reactor failed to provide one-step reformer. The multiple temperatures could provide basic information that could be used to optimize the water-shifting of the CO. However, due to lack of resources, the temperature distribution of the first reactor was not monitored, and neither was the use of the second reactor (for water-shifting).

The tests were carried out with a small plasmatron, and the power was limited by the limitations of the hood in which the experiments were performed. Larger plasmatrons, better reactor thermal insulation, efficient heat regeneration and improved plasma catalysis could play a major role in specific energy consumption reduction and increasing the methane conversion.

Preheating (evaporation!) of diesel provides better process parameters compared with injection of diesel without preheating. The specific energy consumption for H_2 production is higher than under CH_4 processing due to low H_2 yield under CO conversion. This is due to limitations in reactor design, as water shifting the CO is relatively easy. If it is assumed that the CO is converted into H_2, then the specific energy consumption for hydrogen production is similar to that from CH_4. This is the case even though diesel has reduced hydrogen content per carbon atom than CH_4. In other words, even though it is easier to reform diesel than methane, the energy expenditure per hydrogen is the same as in methane due to the fact the hydrogen content in diesel is smaller.

In future work, the following systems will be explored:

- improved process equipment design
- external boiler for water vapor production
- usage of alternative catalysts
- improved fuel/water injection, with maximal atomizing of liquid diesel.

5. Conclusion

Good reforming, with no noticeable soot production, was obtained. The specific energy consumption was equal to that previously obtained with methane reforming, with much reduced concentration of methane in the reformate.

References.

[1] Bromberg, L., Cohn, D. R., and Rabinovich, A., *Plasma Reformer/ Fuel Cell Systems for Decentralized Power Applications*, *Int. Journal of Hydrogen Energy*. **22** 83 (1997)

[2] Bromberg, L.; Cohn, D.R.; and Rabinovich; A.; *Plasma Reforming of Methane*, *Energy and Fuels* **12**, pp. 11-18 (1998)

[3] L. Bromberg, D.R. Cohn, A. Rabinovich and N. Alexeev, *Plasma Catalytic Reforming of Methane*, accepted for publication, *Int. J. Hydrogen Energy*

[4] Trusov B.G. *Application of the Variational Principle for Solving Problems, Chemical Kinetics - Doklady Physical Chemistry*, .**339**, N.4-6, 1994, pp.239-242. Translated from Doklady Akademii Nauk, **339**, No.6, pp.771-775 (1994)