Proceedings of the 1998 U.S. DOE Hydrogen Program Review

NREL/CP-570-25315

Plasma Catalytic Reforming of Methane

L. Bromberg, D.R. Cohn, A. Rabinovich
MIT Plasma Science and Fusion Center
Cambridge, MA 02139

and

N. Alexeev
Baikov Institute of Metallurgy
Russian Academy of Sciences
Moscow, Russian Federation

ABSTRACT

Thermal plasma technology can be efficiently used in the production of hydrogen and hydrogen-rich gases from methane and a variety of fuels. This paper describes progress in plasma reforming experiments and calculations of high temperature conversion of methane using heterogeneous processes. 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 disociation and substantial degree of ionization. The high temperatures accelerate the reactions involved in the reforming process. Hydrogen-rich gas (50% H_2, 17% CO and 33%N_2, for partial oxidation/water shifting) can be efficiently made in compact plasma reformers. Experiments have been carried out in a small device (2-3 kW) and without the use of efficient heat regeneration. 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. Larger plasmatrons, better reactor thermal insulation, efficient heat regeneration and improved plasma catalysis could also play a major role in specific energy consumption reduction and increasing the methane conversion. A 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.

I. Introduction

Manufacturing of hydrogen from hydrocarbon fuels is needed for a variety of applications. These applications include fuel cells used in stationary electric power production and in vehicular propulsion. Hydrogen manufacturing is also needed for industrial applications and could be used in refueling stations for hydrogen powered vehicles. There is a wide range of requirements on the capacity of the hydrogen manufacturing system, the purity of the hydrogen fuel, and capability for rapid response.

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 hydrogen production from heavy hydrocarbons.

The main disadvantages of plasma reforming are the dependence on electrical energy and the difficulty of high-pressure operation (required for processes that require high pressure, such as ammonia production). Dependence on electrical energy results in energetics that are less favorable than purely thermal processes, specially for endothermic reforming reactions such as steam reforming. High pressure, while achievable, increases electrode erosion and decreases electrode lifetime.

Plasma devices referred to as plasmatrons can generate very high temperatures (>2000 C) with a high degree of control, using electricity. The heat generation is independent of reaction chemistry, and optimum operating conditions can be maintained over a wide range of feed rates and gas composition. Compactness of the plasma reformer is ensured by high energy density associated with the plasma itself and by the reduced reaction times, resulting in short residence time. Hydrogen-rich gas can be efficiently produced in plasma reformers with a variety of hydrocarbon fuels (gasoline, diesel, oil, biomass, natural gas, jet fuel, etc.) with conversion efficiencies into hydrogen-rich gas close to 100% (1,2).

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. 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 and with "dirty" hydrocarbons

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]. It could also be used for mobile applications (e.g., on-board generation of hydrogen for fuel cell powered vehicles) and for refueling applications (stationary sources of hydrogen for vehicles).

A previous paper [2] presented results of plasma conversion of methane, using partial oxidation (air as the oxidizer), steam reforming (water) and pyrolytic reforming (no oxidizer). Results for homogeneous operation, and preliminary results of plasma catalysis were reported in that paper.

In this paper, further optimization of plasma catalysis is described as a means to decrease the electrical requirements. The energy requirement, the hydrogen conversion, and the use of a one-step reforming/water shift reactor are investigated as a function of the plasma parameters. Section II briefly describes calculations of the homogeneous process using the method of non-equilibrium thermodynamics. Section III briefly describes the experimental results with methane. Preliminary costs projection are described in Section IV. Finally, the conclusions are summarized in section V.

II. Computer Simulation by methods of non-equilibrium thermodynamics

In this section, the process of partial oxidation of methane is investigated using the method of non-equilibrium thermodynamics [3]. The method is based on the *extreme principle* that assumes that the entropy increases at the maximum rate. Together with the laws of non-equilibrium thermodynamics, it allows to determine quantitatively a trajectory of chemical process and changes of reactants concentrations in any gaseous systems. This new technique of chemical kinetics simulation has been used to determine the reaction trajectory of methane high temperature partial oxidation in an adiabatic reactor.

The partial oxidation/water shifting reagents are mixed according to the ratio

$$CH_4 + 0.5\ O_2 + 1.88\ N_2 + H_2O$$

Figures 1-3 show results of the calculations for initial temperatures of 500 K, 1500 K and 2000 K.. It was found that:

- reaction trajectory may be divided into two stages
    - during the first stage, complete combustion of part of methane occurs, producing mainly CO_2 and H_2O and substantially increasing the temperature of the system;
    - during the second stage, reactions of the remaining methane with CO_2 and H_2O occur providing H_2 and CO production and decreasing the temperature of the system;
- at low initial temperatures (500 K), the "length" of the trajectory of combustion (first stage) is very small compared with methane reactions with H_2O and CO_2;

- an increase of the initial temperature decreases the difference between length of the trajectory of combustion (first stage) and reforming reactions (second stage).

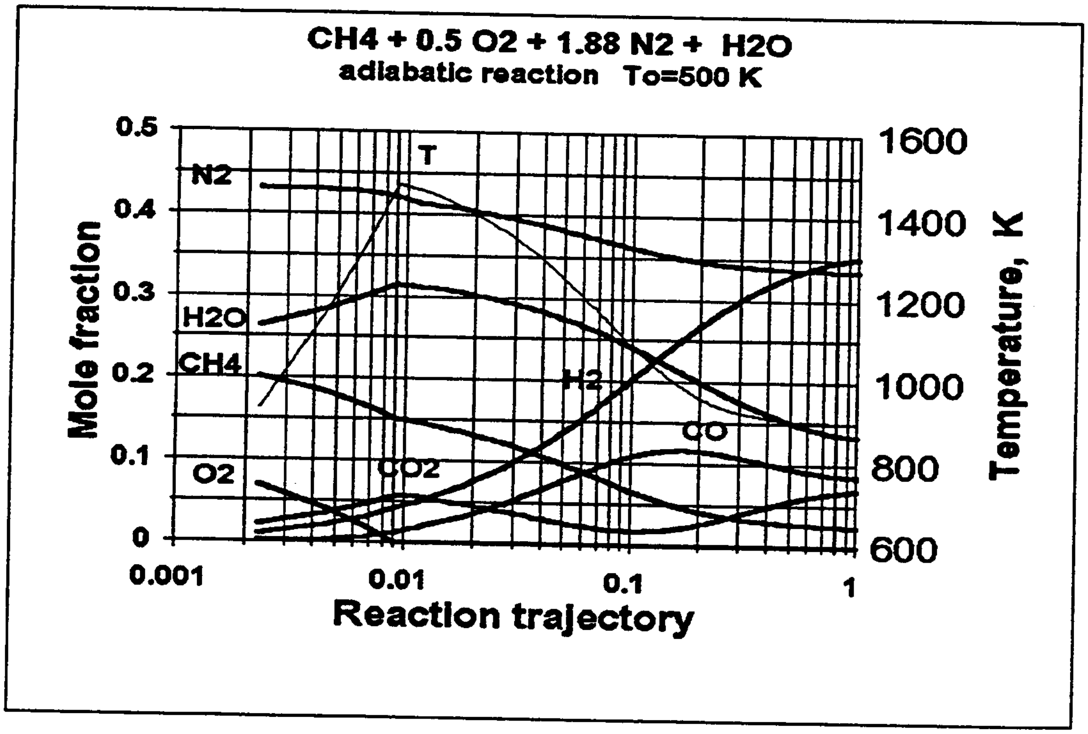

Figure 1. Reaction path for methane reforming, with initial mixture $CH_4/O_2/N_2/H_2O$ or 1/.5/1.88/1. Initial temperature of mixture is 500 K

These results of the simulation correspond to the well known *two-step kinetic* model of hydrocarbon partial oxidation process. However, these results have been obtained without the use of kinetic data.

The use of the plasma in plasma catalysis affects both stages. The plasma process accelerates the reactions, preparing the hydrocarbon-air mixture for the catalytic phase. In addition, although not considered in this paper, this process should be very efficient for heavier hydrocarbons. The heavier hydrocarbons are converted in the plasma phase into lighter hydrocarbons that are easily processed by the catalytic phase.

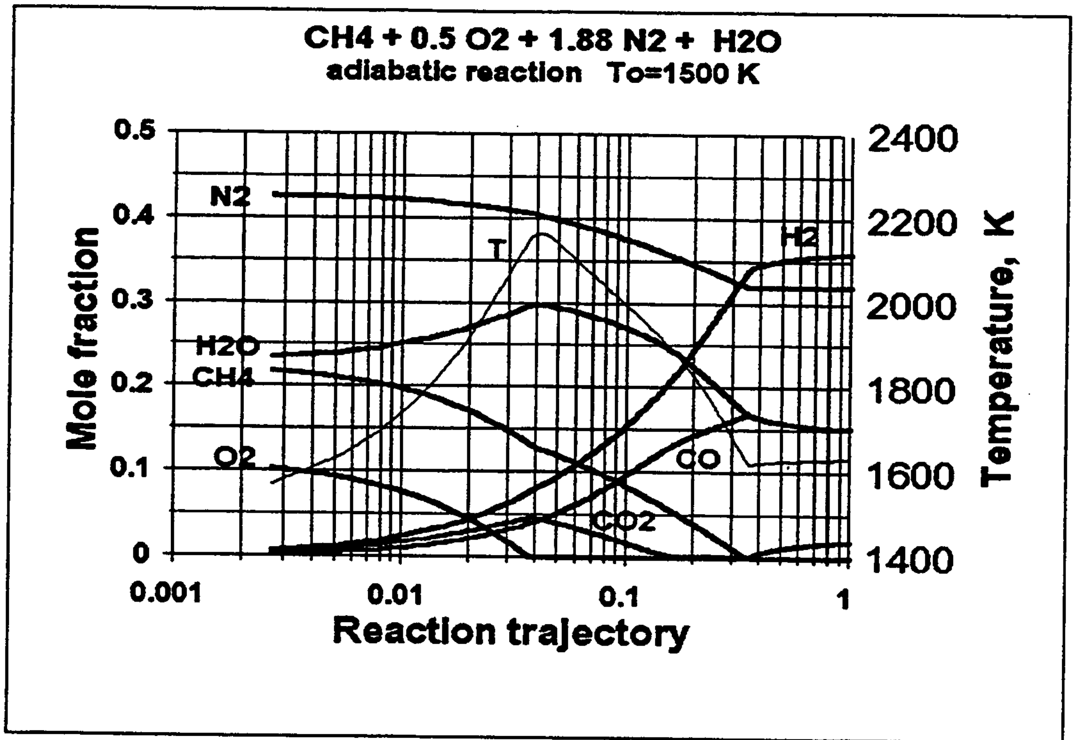

Figure 2 Same as Figure 1, but for initial temperature of mixture of 1500 K

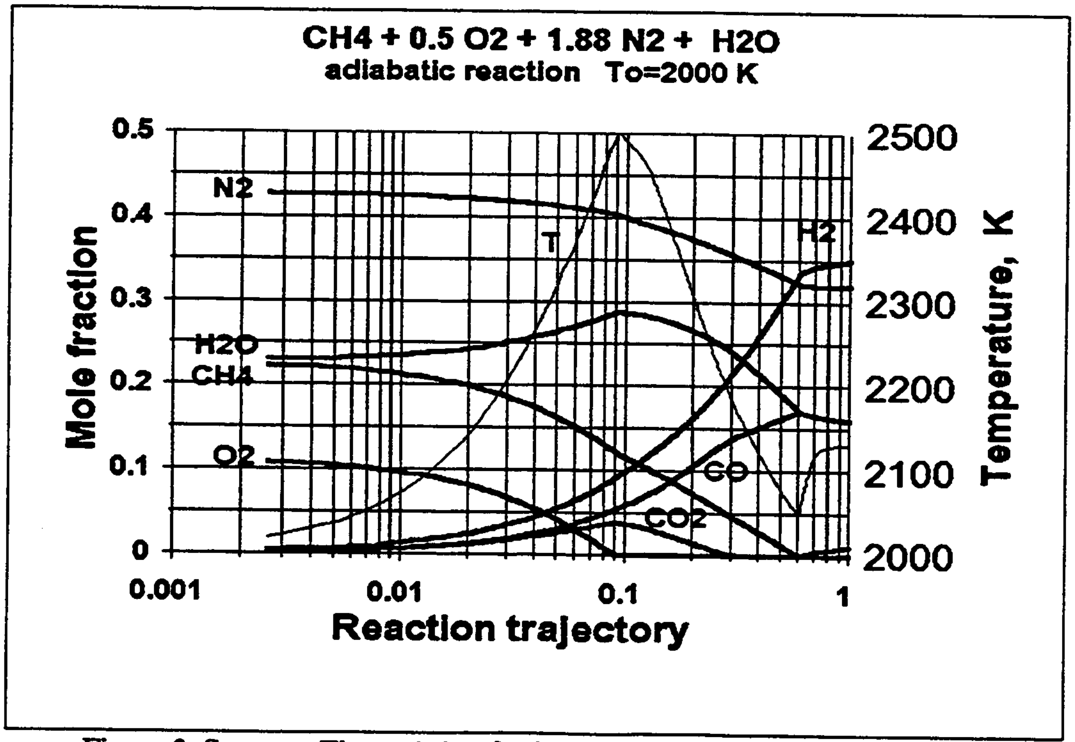

Figure 3 Same as Figure 1, but for initial temperature of mixture of 2000 K

III. Experimental investigations

The experiments with methane were carried out with a system similar to that described in [2]. 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 plasmatron operated on conventional building compressed air. Bottled methane was used for the experiments. 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. No NOx is expected because of the highly reducing product gas. Similarly, no HCN or CN's are expected because of the presence of an oxidizer, which binds the carbon as CO or CO_2, instead as CN.

The following basic process parameters are varied in experiments:

- power input (plasma enthalpy);
- air/CH_4 and H_2O/CH_4 ratios;
- total throughput

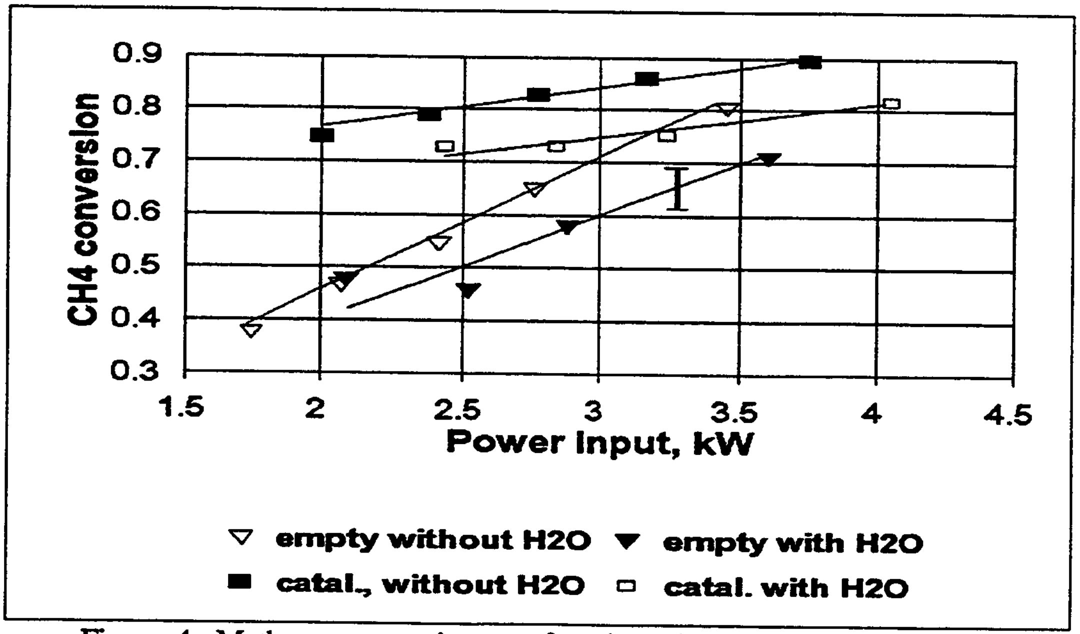

Figure 4. Methane conversion as a function of the Power input to the reactor for constant methane flow rate.

Figure 4 shows the hydrogen yield as a function of the power input. Methane conversion depends strongly on power input, especially for homogeneous reaction. Under low value of power input homogeneous plasma process provides low conversion of methane about 40%. The use of stationary catalyst bed makes possible to increase methane conversion up to 75 % even at the lowest values of input power.

In principle, a homogeneous reactor may provide conversion of methane more than 80%, but the power input is high (more than 100 MJ/kg H_2).

The downstream addition of water vapor into the methane-air mixture decreases the methane conversion and the hydrogen yield.. Hydrogen yield is maximized, and the specific energy consumption is minimized when the water is added together with the methane and the non-plasma air.

A feature of plasma catalytic reactions is the low CO content in the products with a one-stage process. CO content in reaction product is about 1.5-3 vol.%, with hydrogen content ~40%. Water vapor excess in the initial gas mixture is required to obtain low CO concentration in the products. However, injection of water vapor downstream from the plasma, in the of catalyst bed, has little effect on the hydrogen yield.

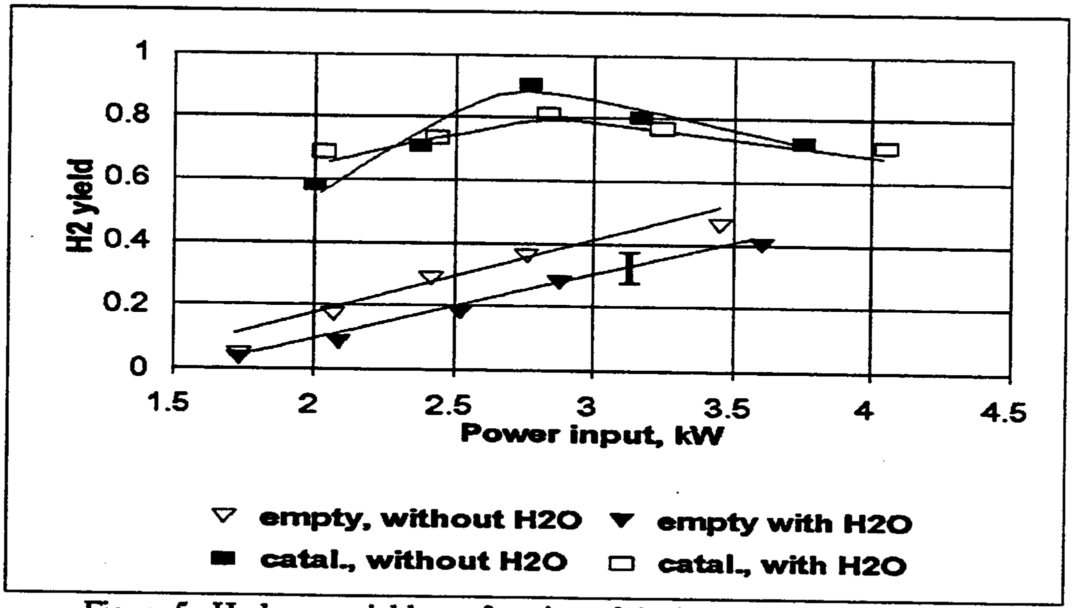

Figure 5. Hydrogen yield as a function of the input power, for constant methane flow rate.

Figure 5 shows the corresponding values of the hydrogen yield (Hydrogen released to hydrogen content in methane). The hydrogen yield in the homogeneous process increases monotonically with power input. The hydrogen yield in the case of the heterogeneous reaction is more complex. The hydrogen yield has a broad maximum for given power input, as shown in Fig.5. The presence of this maximum may be explained by an increase in the of reaction temperature at the higher input powers. This shifts the reaction $CO+H_2O \Leftrightarrow CO_2+H_2$ to the production of CO and H_2O.

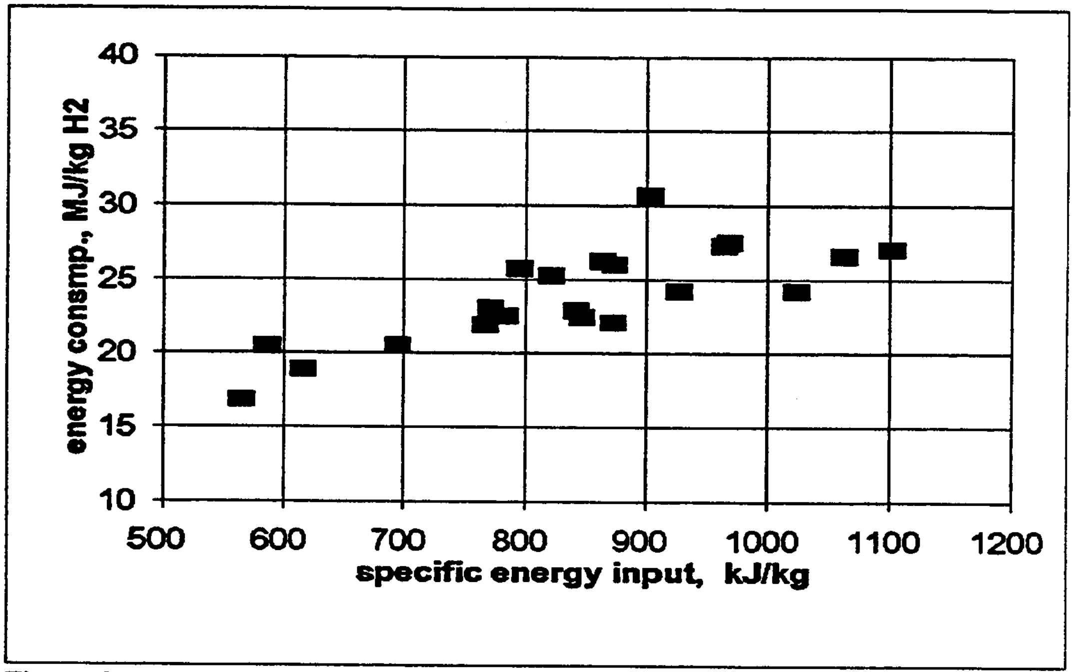

Figure 6. Hydrogen specific energy consumption as a function of the specific energy input

Figure 6 shows the specific energy consumption as a function of the specific energy input. The specific energy consumption is defined as the ratio of the electrical power to the hydrogen throughput of the product gas. The specific energy input is the ratio of the electrical power to the total mass throughput. Plasma catalytic process decreases the required specific energy consumption to less than 17 MJ/kg H_2. Under such conditions, the calculated mean temperature of the unreacted methane/air/water mixture is about 750 - 800 K. This temperature corresponds to the required initial temperature for the autothermal conversion of methane in conventional catalytic reformers. The specific energy consumption can be readily compared with the heating value of the produced hydrogen, 120 MJ/kg H_2 (LHV).

The presently achieved composition and specific energy requirement of catalytic plasma reforming are shown in Table 1.

Table 1. Composition, yield and specific energy consumption for methane reforming using plasma catalysis.

H2		35%
CH4		5%
CO		3.7%
CO2		15%
N2		41%
Methane conversion		70%
Specific energy consumption	(MJ/kg H2)	16

Further decrement of the specific energy consumption may be achieved through the use of a heat exchanger to preheat the input reagents using the enthalpy of the product gases, as well as with reactor design and process parameters optimization. The reactor design can be further optimized by the use of improved heat insulator in conjunction with new types of catalysts. Optimization of the process parameters involves the increase of methane conversion excluding increase of power input by variation of initial mixture composition and methane space velocity.

Figure 7 shows the corresponding hydrogen yield. The hydrogen yield increased by a factor of 2 from those of the homogeneous reactions, as reported in 1997 [2]. Decreasing the specific energy consumption has not decreased the hydrogen yields from those reported in 1997 [2]. The hydrogen yield is shown in Figure 7 as a function of the total energy consumption, for a large number of experiments at different powers and different throughputs.

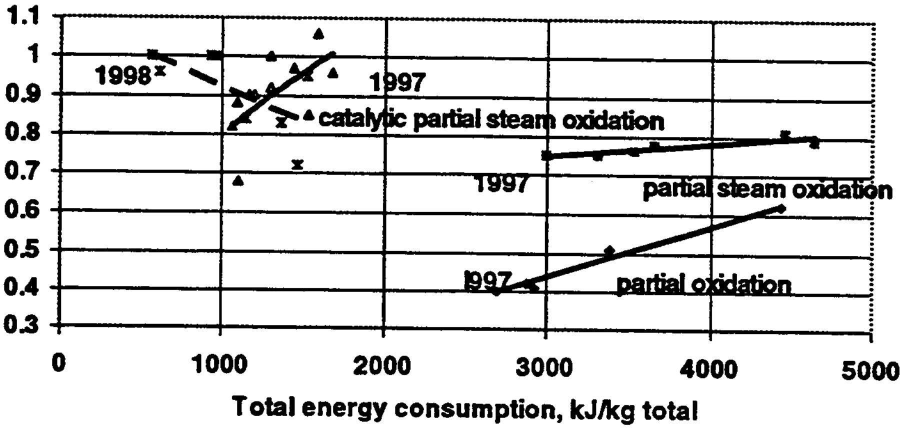

Figure 7. Hydrogen yield for plasma reforming of methane, as a function of the total energy consumption.

The progress in minimization of specific energy consumption is demonstrated in Fig 8. The specific energy consumption is shown in the figure as a function of the total energy consumption. The specific energy consumption decreased by a factor of 3 from those of homogeneous reactions, as reported in 1997 [2]. Since then, the specific energy consumption has decreased by another factor of 3 since, to less than 17 MJ/kg H_2.

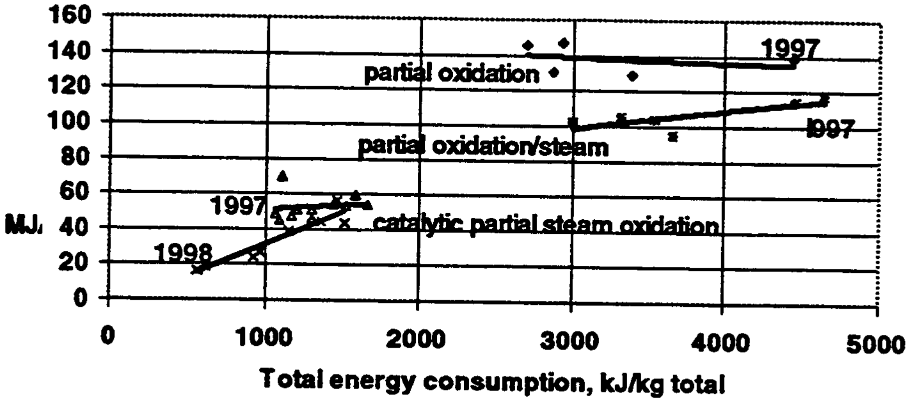

Figure 8. Specific energy consumption for hydrogen manufacturing from methane, as a function of the total energy consumption.

IV. Hydrogen costs

Although preliminary, it is useful to determine the costs of hydrogen manufacturing using a plasma reformer.

There are three major costs in the manufacturing of hydrogen-rich gas. There is the cost of the natural gas, the cost of the electricity, and the capital costs of the plasmatron reactor system. In addition, there is the need of gas cleanup, reducing the CO, CO_2 and N_2 contents. In this section, the costs of producing the clean gas are presented, and only rough costs of the gas cleanup process are described.

For the calculations, it is assumed that the optimized process can produce hydrogen at an specific energy consumption of 8 MJ/kg H_2.

This number is a factor of two lower than the one that has already been achieved. It is expected that the process can be improved through the use of a heat exchanger and through further optimization of the process, as described in the previous section.

It is estimated that the cost of the plasmatron system in about \$0.5 per W of electrical power. This includes the cost of the power supply and the plasmatron. Spare parts are additional, with a lifetime of 1000 hours. The cost of the system is actually not linear with power, but less than linear. Thus larger systems will produce hydrogen at lower costs than what is presented here.

The methane cost is assumed to be \$0.1/m^3 (\$2.6/MMBTU). Finally, the cost of the electricity is assumed to be \$0.05/kWhr.

It is assumed that the capital equipment is depreciated over a three year period, a conservative assumption since the power supply and ancilliary systems will last substantially longer.

The capital and operating costs of hydrogen-rich gas manufacturing are shown in Figure 9 as a function of the specific energy consumption. For a specific energy consumption less than ~20 MJ/kg H_2, the cost of the electricity and plasma/reactor equipment is substantially lower than the cost of the natural gas, and further decreases in the specific energy consumption do not decrease substantially the cost of the hydrogen-rich gas.

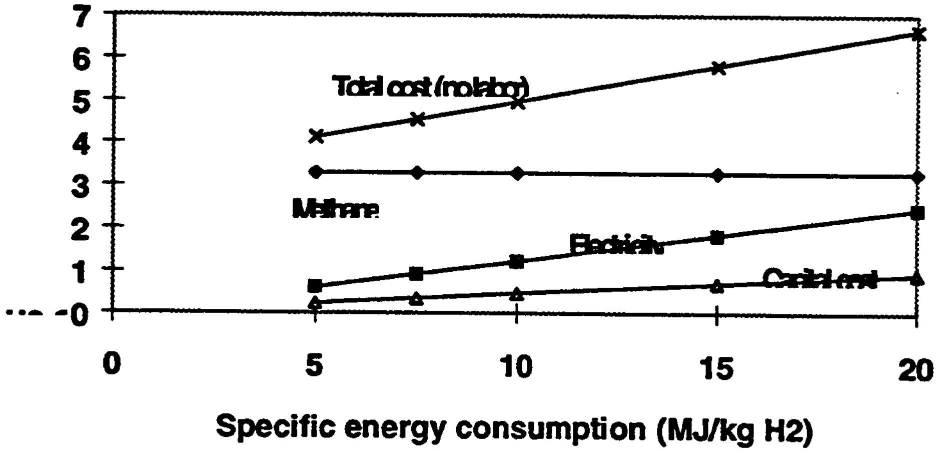

Figure 9 Contributors to cost of manufacturing hydrogen as a function of the specific energy consumption.

Table 2 shows the items associated with the cost of generating hydrogen-rich gas, assuming 8 MJ/kg H_2. If the cost of gas cleanup is less then \$5/MMBTU, then the cost of generating hydrogen, even at the low production rates assumed, is less than \$10/MMBTU.

Table 2. Distribution of costs of manufacturing hydrogen rich gas from methane using plasma catalysis, in \$/MMBTU H_2

Methane cost	**\$3.28**
Electricity cost	**\$0.92**
Depreciation cost of equipment	**\$0.35**
Total	**\$4.55**

V. Conclusions

Plasma reforming of methane, specially plasma catalysis, has been demonstrated with sufficiently low energy consumption and with high hydrogen yields to be economically interesting for energy applications.

The obtained results with plasma catalysis indicate hydrogen yields of about 100% (corresponding to about 80% methane conversion) and minimal specific energy consumption. Substantial improvements should be obtained through the use of heat regeneration, improved reactor and optimized residence time.

With water injection, it was possible to combine reforming and water shift reactions in a single stage with no soot buildup on the catalyst or on the surfaces of reactor. The device is very compact, with power densities of ~30 kW (H_2 HHV)/liter of reactor, or ~10 m^3/hr H_2 per liter of reactor.

Plasmatron generation of hydrogen could be used for decentralized energy production with fuel cells. Another one possible applications of this technology is for onboard reforming for the manufacturing of hydrogen rich gases. The compactness of the reformer, with high power densities, makes the technology attractive for this application.

Plasma reforming could also find uses for decentralized hydrogen production, such as in transportation refueling systems, either on-demand generation of hydrogen (requiring 200-500 kW plasmatrons) or small 20 kW CW plasmatrons (with stationary storage) for 30-50 vehicle fleets. The technology could also be used for industrial applications. Finally, plasma reformers could be used with hard to use fuels, such as raw biofuels or heavy oils.

Acknowledgments

This work was performed under the auspices of DOE under contract FG04-95AL88002

References.

[1] Bromberg, L., Cohn, D. R., and Rabinovich, A., *Plasma Reformer/ Fuel Cell Systems for Decentralized Power Applications, Int. Journal of Hydrogen Energy.* Vol. 22, pp. 83-94 (1997)

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

[3] 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)