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Plasma Reformer/Fuel Cell System for Decentralized Power Applications*

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Abstract

A plasma-driven process is described for the reforming of hydrocarbon fuels into hydrogen-rich gases for use in fuel cells. High temperature non-catalytic reforming offers many advantages over thermal catalytic reforming. The high gas temperatures obtained via plasmas reduce the volume and weight of the reformer, due to the fast kinetic rates. In addition, it allows fast response to changing fuel requirements, a characteristic needed in mobile applications. A plasma reformer-fuel cell system could provide a means to increase fuel flexibility and cost reduction of systems for both stationary and mobile fuel cell systems, over a wide range of operating modes. In addition to steam reforming and partial oxidation, thermal decomposition could be used to provide hydrogen-rich gas with greatly reduced production of carbon dioxide. Plasma reformer-fuel cell systems could utilize a wide range of hydrocarbon fuels, including diesel, gasoline, biomass, natural gas and alcohols.

Nomenclature

ΔH	the required enthalpy addition, starting from a
	mixture at room temperature
η_s	overall system efficiency
Preformer	ratio between reformate HV and the hydrocarbon fuel HV
η_{fc}	fuel cell efficiency
R	ratio of reformate combustion enthalpy to ΔH
η_{plasma}	plasmatron efficiency
ε	recirculating energy fraction

1 Introduction

By converting chemical energy directly into electricity, the fuel cell offers potential advantages of high efficiency (up to 60%), compactness, modularity, and low atmospheric pollution [1, 2]. Fuel cell technology could be particularly important in the development of decentralized power sources and for mobile applications, such as on-board vehicles. The decentralized power sources could be used in a variety of settings including remote locations, congested urban locations, and in commercial and military applications, while the on-board reformer may allow vehicles to operate on hydrocarbon fuels with drastically diminished emissions.

A major factor in developing fuel cell systems is the requirement for hydrogen-rich gas fuel. Fuel cell applications could be enhanced if the fuel cells could be readily used with a range of relatively inexpensive, readily available, and easily transportable hydrocarbon fuels. High-temperature fuel cells (molten carbonate at 650 C and solid oxide at 1000 C) can produce the required hydrogen-rich gas from natural gas inside the fuel cell (internal reforming). However, natural gas is not available at remote locations. Alternatively, hydrogen-rich gas could be obtained from various hydrocarbons using external catalytic reformers. If hydrocarbon fuels heavier than methane and methanol are used, such as gasoline, oil, diesel, etc., internal and external reforming could cause carbon deposits, plugging problems, and contamination of the catalysts and/or electrodes. Due to the slow reaction rates at the operating temperature, external reformers are heavy, large, have slow response, use expensive catalyzers, and limit the range and impurity level of the hydrocarbon fuels. Special handling and combustion of fossil fuel is needed for heating of the reformer, further limiting the options of hydrocarbon fuels. In addition, experimental investigations of both thermal non-catalytic and catalytic pyrolysis by conventional means have not provided sufficiently pure hydrogen gas from diesel and gasoline.

Elimination of these problems may be possible by the use of a plasma reformer in specially optimized plasma reformer-fuel cell systems. The 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 may be maintained over a wide range of feed rates and hydrogen composition. By using high gas temperature, the need for a catalyzer is avoided, minimizing

the size and weight of the reformer (because of the much faster reaction rates at the higher temperatures), and increasing the fuel options. 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 (50-75% H₂; 25-50% CO) can be efficiently made in compact plasma reformers with a variety of hydrocarbon fuels (gasoline, diesel, oil, biomass, natural gas, jet fuel, etc.). Plasma reformers are relatively inexpensive (they use relatively simple metallic or carbon electrodes) and conversion efficiencies of hydrocarbon fuel into hydrogen-rich gas close to 100% have been demonstrated [3, 4]. In addition, it may be possible to use the high degree of control of the plasma reformer to substantially reduce CO₂ emissions.

Plasma reforming of light hydrocarbons (methane and natural gas) has been used in the Huls process [5] for the manufacturing of acetylene. These systems are intended for industrial manufacturing of acetylene and were large, heavy, and not transportable. The Huls plasma processing has been investigated for the manufacturing of H_2 by the steam-reforming of methane [4]. Large systems have been built (initial pilot experiments with a 50-500kW system), with the goal of larger ones. Their reformate gas mixture, optimized for acetylene production (by operating at high gas temperatures), contains more than 60% hydrogen, 17% acetylene, and 7% ethylene. Due to the manufacturing of acetylene and the high temperatures, the process is strongly endothermic and requires large heat input.

Higher hydrogen yields can be achieved by operating at lower temperatures (resulting in less acetylene and ethylene). The temperature of the reactor can be controlled by adjusting the plasma power, the gas throughput and the operating pressure, among others. Moreover, by increasing the hydrogen concentration in the starting reagents (by, for example, recirculating excess hydrogen from the fuel cell), significant narrowing of the temperature range where condensed carbon and acetylene exists can be obtained. A further method of control is through the use of two stage reactors. In the first stage the plasma produces a high enthalpy gas that is used to process a fluid introduced in a second stage. The plasmatron may, for example, operate with water, with the hydrocarbons injected downstream. Hydrogen yields (65% H₂, 35%CO) larger than those from the Huls process have been demonstrated by the work of Rudiak *et al.* [3]. A key feature of the plasma reformer-fuel cell system is that a modest fraction of the electricity produced by the fuel cell is needed to power the plasmatron. The overall system efficiency (conversion of chemical energy to electricity) is high.

Steam, pyrolytic and partial oxidation reforming could be provided by plasma devices.

2 Plasma Reformer-Fuel Cell Systems

In order to optimize the plasma reformer-fuel cell system, an integrated design approach that closely matches the different components is required. High system efficiency is possible due to the combination of low power requirement and high conversion efficiency of the plasmatron in reforming the hydrocarbon fuels and the high efficiency of the fuel cell.

A mass and energy flow diagram for steam reforming is shown in Figure 1. The plasma reformer takes hydrocarbon fuels and water (for steam reforming) and using electricity, generates hydrogen-rich gas (60-75% H₂ and 25-40% CO). It would be advantageous to use a fuel cell that uses this gas mixture directly (a molten carbonate or solid oxide fuel cell). For a fuel cell that can only use H₂ gas, it is possible to use a water shift reaction which converts, with $\Delta H \approx 0$, the CO gas into H₂ and CO₂. It may be possible to complete the water shift reaction in the plasmatron itself by injection of steam beyond stochiometric concentration. Alternatively, it would be possible to inject additional water into the high temperature exhaust gases of the plasmatron.

If R is the ratio between the chemical energy leaving the plasma reformer and the thermal energy externally added to the reforming reaction in the plasmatron, then the net overall system efficiency η_s is given by

$$\eta_{s} = \rho_{reformer} \left(\eta_{fc} - \frac{1}{R\eta_{plasma}} \right)$$

where η_{fc} is the fuel cell efficiency. η_{fc} can be as high as 60%. $\rho_{reformer}$ is the ratio between the heating value of the reformate and the heating value of the hydrocarbon fuels. The value of $\rho_{reformer}$ depends on the hydrocarbon fuel and on the method of reforming (steam reforming, partial oxidation or thermal decomposition). It is in general larger than 1 for endothermic reactions. For exothermic reactions with no externally-added thermal energy, R = 1.

 η_{plasma} is the plasmatron efficiency, defined as the ratio between the gas heating power to its electrical power input. Plasmatrons have been designed with $\eta_{plasma} > 90\%$ [6].

R is calculated by dividing the enthalpy of combustion of the reformate by ΔH (the energy required to drive the reaction at the operating temperature, starting from a mixture at room temperature). R is determined from thermodynamic calculations, and is a property of each fuel.

The recirculating power fraction, ϵ (the ratio between the electric power required to drive the plasmatron to the electric power from the fuel cell) can be readily shown to be given by

$$\epsilon = \frac{1}{R\eta_{fc}\eta_{plasma}}$$

The recirculating fraction, therefore, is a function of the fuel cell and plasmatron efficiencies, and the nature of the hydrocarbon fuel.

3 Thermodynamic Studies

In this section, the thermodynamics of steam reforming, partial oxidation and thermal decomposition are reviewed, and the results applied to plasmatron/fuel cell systems; as described in Section 2.

3.1 Steam Reforming

Thermodynamic analysis [7] shows that for steam conversion of hydrocarbons, the end product contains primarily molecular hydrogen and carbon monoxide at 1000-2500 C. The conversion of hydrocarbons into H₂ and CO is virtually the same for gaseous and liquid hydrocarbons (CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄, C₂H₄) and it is close to 100%.

In the steam conversion mode, hydrogen-rich gas is produced by the reaction

$$C_m H_n + m H_2 O \rightarrow m CO + (\frac{n}{2} + m) H_2 - \Delta H$$

Here ΔH is the energy released (consumed) by the exothermic (endothermic) reaction. For the steam-reforming of most hydrocarbonaceous fuels, the reactions are endothermic, and ΔH is positive.

Typical equilibrium calculations steam reforming of methane, made using the CHEMKIN (CHEMical KINetics) code developed at the Sandia National Laboratory [8], are presented in Figure 2. Figure 2-a shows the molar fractions of the different compounds of a system at equilibrium as a function of the reformate temperature. The corresponding equilibrium enthalpy is shown in Figure 2-b. The calculations were performed at constant pressure (1 bar). Figure 2-a shows that it is possible to have near complete reforming at temperatures lower that 2000 K. Operating at lower temperature decreases substantially the energy requirements, at the expense of slower reaction rates and the possibility of increased condensed carbon. Enthalpy addition requirements ΔH as low as 8 MJ/kg are possible by operating at 1200-1500 K. Similarly, the value of ΔH required to reform higher hydrocarbons at the lower temperatures is about 5-8 MJ/kg, depending on the nature of the hydrocarbon, whether steam or thermal decomposition is used, and the reforming temperature.

In order to optimize the performance of the plasma reformer, relatively constant temperature across the zone heated by the plasma is required. Incomplete conversion with soot formation may result at the lower temperatures, and at the higher temperatures the required heating input is increased. In addition, at temperatures larger than about 2500 K, higher molecular weight hydrocarbons (such as C_2H_2) are created.

Figure 3-a shows the calculated values of R and $\rho_{reformer}$ at equilibrium as a function of temperature for methane steam reforming at atmospheric pressure (corresponding to the case shown in Figures 2-a and b). Again, these results are only illustrative since they do not include the kinetics of the process. The value of R has a maximum around 900 K (at the lower temperatures the hydrocarbon is only partially reformed, while at the higher temperatures ΔH increases faster than the reformate heating value). The maximum value of R is about $R \sim 4.2$. $\rho_{reformer}$ increases with increasing temperature. Figure 3-b shows the calculated overall system efficiency η_s at equilibrium, assuming that $\eta_{fc} = 60\%$ and $\eta_{plasma} = 90\%$.

Table 1 shows the minimum required energy for several relevant hydrocarbons for stochiometric steam reforming. In Table 1 it is assumed that the required ΔH is

determined by the difference between the enthalpy of combustion of the reformate (heating value) and the enthalpy of combustion of the original hydrocarbon fuel. This assumes that the heat capacity of the compounds is small. Then the energy required to bring the compounds to reacting temperature is small compared with their enthalpy of combustion, a good assumption for the temperature range of interest. The required energy input to drive the system (starting from a CH₄-H₂O mixture at 300 K) is ~ 0.23 MJ/mol for CH₄. For gasoline, oil or diesel, with a composition of approximately CH_{1.85}, the corresponding value of ΔH is $\Delta H \sim 0.19$ MJ/mol. Table 1 indicates that R varies from about 4.5 to 7.5 for most hydrocarbons, with extremes of 3 for reforming of carbon (coal gasification) and 14 for reforming of acetylene. The corresponding value of $\rho_{reformer}$ decreases with increasing value of R. For the assumptions made in Table 1 (neglecting the heat capacity of the hydrocarbon fuels and the reformate), R and $\rho_{reformer}$ are related by

$$\rho_{reformer} = rac{R}{R-1}$$

Table 1 also shows the system efficiency η_s for the different fuels, assuming $\eta_{fc} = 60\%$. For CH₄, with R = 4.9 and $\rho_{reformer} = 1.26$, the simple model indicates that $\eta_s = 47\%$ and $\epsilon = 0.38$.

The equilibrium calculations presented here include the presence of soot. Removing the possibility of soot formation (usually referred to as quasiequilibria) does not change the results substantially. The effect of the presence of C(s) on the overall efficiency will be discussed in Section 3.4.

3.2 Partial Oxidation

For partial oxidation, enough air is introduced into the the system to turn all of the carbon into CO using an exothermic reaction,

$$C_n H_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2 - \Delta H$$

With the same assumptions as those in Table 1 for steam reforming, Table 2 shows the results for partial oxidation. The overall efficiency of the system is higher than that of steam reforming, due to the lower energy required to reform the fuel. For a fuel cell efficiency of $\eta_{fc} = 60\%$, the efficiencies of the system for the different hydrocarbons

are reduced to around 50%. For the exothermic reaction, the model assumes that the plasmatron is not necessary. In practice, the efficiency will be reduced due to the finite plasmatron power requirements. However, Table 2 shows the trends for the different hydrocarbon fuels.

The power requirements due to the finite heat capacity of the reactants can be calculated using thermodynamical equilibrium assumptions. These assumptions also determine the composition of the gas mixture. Figure 4 shows the molar fractions as a function of the initial temperature for partial oxidation of methane, with air as the source of oxygen (*i.e.* diluted with nitrogen). Constant pressure and constant enthalpy were assumed. Substantial amounts of CO_2 , C(s) (carbon solid) and H_2O are predicted up to average temperatures of 1500 K. The actual amount of carbon solid will be smaller, due to the relatively slow growth rates of the soot and the short residence in the hot zone. For high quality reformate, high temperatures are beneficial, similar to those results for steam. The higher temperatures required also speed the reactions, necessary because of the brief residence time in these plasma reactors.

Since air is the source of oxygen for partial oxidation, it is necessary to determine the expected levels of NOx in the products. Equilibrium calculations have indicated that only at the highest temperatures is the NO equilibrium concentration above 1 ppm. Just as the non-equilibrium effects help in the case of soot, they may hurt in the case of NOx. However, NOx will probably not be an issue because of the very fuel rich operation. The kinetic calculations are required to address the NOx issue.

Figure 5 shows the temperature of the system (adiabatic) as a function of the initial temperature of the reactants. The temperature increases, due to the exothermic nature of the reaction. For adiabatic conditions with the input gases at room temperature, the product gas reaches about 1000K. The temperature difference between the products and the input reactants, however, decreases with increasing temperature. At the higher temperatures, the energy released during the reaction increases the temperature of the mixture by only ~ 200 K. This means that at the higher temperatures, the bulk of the heating still needs to be performed by external means.

With the use of a heat exchanger, the thermal enthalpy of the reformate can be used to preheat the air that is introduced into the plasmatron. In this way net external heating requirements can be reduced. Partial oxidation may require substantially less plasmatron power than steam reforming or thermal decomposition. Thus the net system efficiencies can be considerable higher.

3.3 Thermal Decomposition for Minimization of CO₂ Emissions

Another option, substantially less well established than partial oxidation and steam reforming, is operation in a water and oxygen free mode, producing nearly pure hydrogen which could be used in a wide range of fuel cell operations.

In thermal decomposition, carbon (soot) and hydrogen are produced by the reaction:

$$C_m H_n \rightarrow mC + \frac{n}{2} H_2 - \Delta H$$

For thermal decomposition of various hydrocarbons, the principal components over a wide range of temperatures (1000-2000 C) consist of condensed carbon and hydrogen. If the condensed carbon is removed from the system and is not burned, production of CO and CO_2 is eliminated. However, it is necessary to dispose of the carbon.

For thermal decomposition of CH₄, $\rho_{reformer} \sim 0.7$, as the heating value of the solid carbon is not used. The corresponding value of R is substantially larger than for steam reforming. R is negative for some hydrocarbons, indicating an exothermic reaction. Table 3 shows the results for thermal decomposition. For those cases where the reactions are exothermic, the overall system efficiency was estimated from $\eta_s = \rho_{reformer}\eta_{fc}$. This relation can be readily derived from the system picture shown in Figure 1, assuming that the electrical drive for the plasma reformer are minimal. It is assumed that for the plasma reformer-fuel cell system the energy released by the reforming reaction is not utilized. As expected, $\rho_{reformer}$ is less than 1 for all fuels considered. This is due to the fact that the condensed carbon is not used.

In comparison to the steam reforming and partial oxidation, the thermal decomposition results in lower overall efficiencies ($\eta_s = 30\%$ for CH₄). However, the plasma reformer/fuel cell system has lower recirculating power, $\epsilon = 0.20$ (vs 0.38 for steam reforming of CH₄). This results in lower capital equipment, at the expense of higher operating costs (due to decreased fuel efficiencies). In the case of thermal decomposition, some of the reaction are exothermic. This is the case for acetylene. The use of this fuel may be useful for small, portable applications. In the thermal decomposition mode of operation, it may be possible to virtually eliminate carbon dioxide emissions. The soot that is produced needs to be separated from the hydrogen-rich gas in a manner that would not plug up the system. Possible commercial uses and methods of disposal of the generated soot are being investigated. Relatively high system efficiency can be obtained even with moderate values of R due to the high value of η_{fc} .

3.4 Comparison Between Reforming Technologies

The above models can be used to estimate the overall efficiencies of a plasmatron/fuel cell system, for different reforming technologies. The comparison presented here assumes methane reforming, with equilibrium composition and with a fuel cell with uniform efficiency ($\eta_{fc} = 0.60$). In reality, it is likely that different reforming technologies are better suited to different fuel cell technologies, with different efficiencies. Such a comparison will have to wait until the actual reformate composition is determined from kinetics modeling and from experiments.

The efficiency of a plasmatron/fuel cell system is shown in Figure 6 for steam reforming, partial oxidation and thermal decomposition, as a function of temperature of the reformate. Two cases are shown for partial oxidation, equilibrium (with C(s)) and quasiequilibrium (without C(s)). The highest overall efficiency are for partial oxidation, with the quasiequilibrium efficiency almost as high as that of the fuel cell itself. The lowest temperature corresponds to the case where there is no additional input of heat, utilizing the energy from the exothermic reaction (adiabatic partial oxidation). Without the formation of C(s), the only inefficiency in the system is the small energy required for the reaction (marginally endothermic). Steam reforming is less efficient than partial oxidation with soot production.

At the lower temperatures, the efficiency for all reforming methods is non-optimal because of incomplete conversion. As the temperature increases, the conversion increases. The heating value of the reformate increases faster than the energy expenditure. After the optimal temperature, the energy expenditure increases faster than the energy from the reformate, and the overall efficiency drops.

Thermal decomposition results in the lowest overall efficiency, due to the fact that the energy in the carbon of the hydrocarbon fuel is not utilized.

4 Plasma Reformer Technology for Electric Power Generation Applications

Application of plasma technology for electric power generation systems requires a level of plasmatron powers of ~ 1 kW for the smallest units to 1000 kW for the larger unit. Lower power plasmatron operation can be obtained by using intermittent operation of a $\sim 1-2$ kW plasmatron.

Table 4 shows results from estimates of the requirements and performance of a plasma reformer-fuel cell system when operated on CH₄ fuel. The numbers are comparable to those of other fuels. When combined with a fuel cell with an optimistic, but realizable efficiency of $\eta_{fc} = 60\%$, the overall efficiency of the system is 47%.

The characteristics of 1 kW, 10 kW, 100kW, and 1000 kW plasma steam-reformer systems are given in Table 5. This Table assumes $\eta_{fc} = 60\%$, $\eta_{plasma} = 90\%$, R = 4.3, and $\rho_{reformer} = 1.3$. Similarly, Table 6 shows the results for plasma thermal decomposition reformer systems. The Table assumes $\eta_{fc} = 60\%$, $\eta_{plasma} = 90\%$, R = 9.03, and $\rho_{reformer} = 0.63$. The net result of not producing CO₂ (in the system with thermal decomposition reforming) is a net drop in efficiency from about 45% to about 30%.

The plasma reformer is highly compatible with different kinds of fuels and fuel cells. It could operate as a steam reformer producing H_2 and CO (which could be used in molten carbonate fuel cells (MCFC), Solid Oxide Fuel Cells (SOFC), and possibly in Phosphoric Acid Fuel Cells (PAFC).

The fuel cell systems that are presently under consideration for power generation applications are the PAFC using hydrogen fuel that is transported to the power station from an external source or is produced at the power plant in a special reformer, and the MCFC and the SOFC using either hydrogen or internally reformed natural gas. The PAFC technology is the most developed and is tolerant to carbon dioxide. However, the PAFC lacks the capability for internal reformation, has relatively low power density, and some of its components are insufficiently stable. The MCFC is now approaching utility demonstration in a 100kW scale unit. EPRI has chosen the 2MW MCFC unit as most suitable for urban needs [2]. Because of the high operating temperature, hydrogen and carbon monoxide may be used as fuels for the MCFC.

In plasma reformer-fuel cell systems, the plasma reformer could potentially pro-

duce hydrogen for the PAFC using a range of hydrocarbon fuels. The requirement for transportation and storage of hydrogen would be eliminated. Moreover, by operating in the thermal decomposition mode, CO_2 emissions could be virtually eliminated.

Combination of the plasma reformer with the MCFC and SOFC should result in very compact and simple systems. Either the steam conversion, thermal decomposition or partial oxidation modes could be utilized. Plasma steam reforming could be very compatible with the MCFC because it almost completely converts hydrocarbon fuels into H_2 and CO. It can be estimated that the necessary space for a nominal 20kW molten carbonate fuel cell plant is less than 45 square feet [2]. The required 2-3 kW plasmatron would have an external diameter of 0.1 m (0.3 ft) and an overall length of 0.2 m (0.6 ft).

The combination of the plasma reformer with the SOFC is also potentially attractive. The SOFC is compact, lightweight, and operates at 900-1000 C. Because the electrolyte is solid, the electrolyte management problems associated with the PACF and the MCFC are eliminated. In the case of using the SOFC, such construction promises to be more compact and lightweight than for the MCFC.

The plasma reformer-MCFC and the plasma reformer-SOFC systems could use the exit hot gas from the fuel cell to heat the gases at the plasma reformer inlet, thus increasing the overall efficiency. In the case of high temperature fuel cell operation (such as for the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC)), the hydrogen-rich gas can be introduced hot from the plasma reformer into the fuel cell. In addition, since the exhaust gas is also hot, the exhaust gas could be used in a topping cycle (via a heat exchanger), or could be used to preheat the reactants.

The plasma reformer and the fuel cell are electrically compatible in that their voltages are comparable (~ 100 V). The plasmatron can be driven directly by the fuel cell.

The plasmatron could be operated either continuously or in an intermittent mode where hydrogen-rich gas is stored. Operation in an intermittent mode would be attractive for low power applications (< 2 kW) where continuous operated plasmatron power levels would be too low for optimum plasmatron operation.

The plasma reformer-fuel cell system would also be useful for load following in utility applications. During base load operation, a power plant could run at nominal load. The extra power could be used by the plasma reformer to produce hydrogen which could be stored in a separate tank. During peak load hours, the stored hydrogen could be routed to a fuel cell or burner.

5 Compact Plasmatron Technology

The plasmatrons can generate very high temperatures (≈ 2000 C) with a high degree of control. The heat generation is independent of reaction chemistry, and optimum operating conditions may be maintained over a wide range of feed rates and hydrogen composition.

An illustrative design of a plasmatron with power of 200-500 kW and a flow rate of 40 - 10000 m³/h is shown in Figure 7 [6]. Basically, the illustrative plasmatron comprises two water-cooled metallic tubular electrodes connected by a vortex generating gas injection chamber [4]. A spark occurs in the gap between electrodes, and the incoming feedstock gas immediately blows the arc from the gap into the interior of the arc chamber. There it is rotated at speeds of up to 1000 revolutions per second by interaction of the arc current with a magnetic field set up by a ferromagnetic circuit using permanent magnets or electromagnets. This type of plasmatron is simple, reliable, and can operate on any kind of working gas. To work in a thermal decomposition mode, it could be equipped with an additional coke filter or dry cyclone for soot separation.

This and numerous other examples show high efficiency and availability of plasma technologies for producing hydrogen-rich gases. Plasmatron electrodes would be made of metal, would last about 2000 hours, and would be readily changeable.

A diagram of a plasmatron that could be used as a plasma steam reformer at lower powers is shown in Figure 8. It has a concentric metallic anode/cathode arrangement. The cathode is the outer electrode. The arc rotates at a high frequency, driven by the interaction between the arc current and the imposed magnetic field. The magnetic field can be provided by an electromagnet or by permanent magnets to minimize power consumption. The water is injected below the arc, and the hydrocarbons are injected beyond the arc, to minimize the formation of carbon deposits on the electrodes. We expect that it will perform well in the 2 - 10 kW power range.

6 Conclusions

The use of a plasma reformer in specially optimized plasma reformer-fuel cell systems would serve as an attractive solution to the issue of hydrocarbon fuel reforming for the production of hydrogen-rich gases for fuel cells and other applications. The plasma reformer uses electricity to heat the gases to high temperatures, resulting in fast reaction rates. The plasma reformer avoids the need for a catalyzer, minimizing the size and weight of the reformer, and increasing the fuel options. Hydrogen-rich gas (50-75% H₂; 25-50% CO) can be efficiently made in compact plasma reformers with a variety of hydrocarbon fuels (gasoline, diesel, oil, biomass, natural gas, jet fuel, etc.). Plasma reformers would be relatively inexpensive (they use relatively simple metallic or carbon electrodes) and conversion efficiencies of hydrocarbon fuel into hydrogen-rich gas close to 100% have been demonstrated. A key feature of the plasma reformer-fuel cell system is that a modest fraction of the electricity produced by the fuel cell is needed to power the plasmatron. The overall system efficiency (conversion of chemical energy to electricity) remains relatively high. In addition, by operating at high temperature without steam or oxygen (thermal decomposition reforming), the plasma reformer can be utilized to virtually eliminate carbon monoxide and dioxide emissions. In the CO_2 elimination mode (thermal decomposition), the plasma reformer/fuel cell system has lower overall system efficiencies as compared with steam reforming, due to lack of carbon oxidation. However, the increased operating cost of the thermal decomposition reformer is partially offset by reduced recirculating power.

Hydro-	Mol.	HV of	HV of	Required	R	ρ	η
Carbon	Mass of	Hydrocarbon	Reformate	Energy			
	Reformate	(kJ/mol)	(kJ/mol)	(kJ/mol)			
C	30	393	560	167	3.353	1.425	0.383
CH ₄	34	890	1120	230	4.870	1.258	0.468
CH₄O	32	726	840	114	7.368	1.157	0.520
C_2H_2	62	1301	1400	99	14.141	1.076	0.561
C_2H_4	64	1411	1680	269	6.245	1.191	0.503
C_2H_6	66	1560	1960	400	4.900	1.256	0.469
C_3H_4	94	1937	2240	303	7.393	1.156	0.520
C ₃ H ₆	96	2058	2520	462	5.455	1.224	0.485
C_3H_8	98	2219	2800	581	4.819	1.262	0.466
C_6H_6	186	3268	4200	932	4.506	1.285	0.454
C ₇ H ₁₆	226	4817	6160	1343	4.587	1.279	0.458
C ₈ H ₁₆	256	5470	6720	1250	5.376	1.229	0.483

Table 1: Steam Reforming of Several Hydrocarbons.

Hydro-	Mol.	HV of	HV of	Required	ρ	η
Carbon	Mass of	Hydrocarbon	Reformate	Energy		
	Reformate	(kJ/mol)	(kJ/mol)	(kJ/mol)		
С	28	393	280	-113	0.71	0.43
CH ₄	32	890	840	-50	0.94	0.57
CH ₄ O	32	726	840	114	1.16	0.52
C_2H_2	58	1301	840	-461	0.65	0.39
C_2H_4	60	1411	1120	-291	0.79	0.48
C_2H_6	62	1560	1400	-160	0.90	0.54
C ₃ H ₄	88	1937	1400	-537	0.72	0.43
C ₃ H ₆	90	2058	1680	-378	0.82	0.49
C ₃ H ₈	92	2219	1960	-259	0.88	0.53
C ₆ H ₆	174	3268	2520	-748	0.77	0.46
C7H16	212	4817	4200	-617	0.87	0.52
C ₈ H ₁₆	240	5470	4480	-990	0.82	0.49

Table 2: Partial Oxidation Reforming of Hydrocarbons.

Hydro-	Mol.	HV of	HV of	HV of	Required	R	ρ	η
Carbon	Mass of	Hydrocarbon	Reformate	H2	Energy			
	Reformate	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)			
CH ₄	16	891	953	560	62	9.03	0.63	0.30
C_2H_2	26	1301	1066	280	-235	-1.19	0.22	0.13
C_2H_4	28	1411	1346	560	-65	-8.62	0.40	0.24
C_2H_6	30	1560	1626	840	66	12.73	0.54	0.28
C_3H_4	40	1937	1739	560	-198	-2.83	0.29	0.17
C ₃ H ₆	42	2058	2019	840	-39	-21.54	0.41	0.24
C_3H_8	44	2219	2299	1120	80	14.00	0.50	0.26
C ₆ H ₆	78	3268	3198	840	-70	-12.00	0.26	0.15
C_7H_{16}	100	4817	4991	2240	174	12.87	0.47	0.24
C ₈ H ₁₆	112	5470	5384	2240	-86	-26.05	0.41	0.25

Table 3: Thermal Decomposition of Hydrocarbons.

Heating value (kJ/mol)	890		
	Steam	Partial	Thermal
	Reforming	Oxidation	Decomposition
Reformate			
Mass (kg/mol)	0.034	0.032	0.004
Heating value in C (kJ/mol fuel)	0	0	393
Heating value in CO (kJ/mol fuel)	280	280	0
Heating value in H_2 (kJ/mol fuel)	840	560	560
Total heating value (kJ/mol fuel)	1120	840	953
Enthalpy change, ΔH (kJ/mol fuel)	230	-50	62
R	4.87	N.A.	9.03
Preformer	1.26	0.94	0.63
$\eta_s \ (\eta_{fc} = 60\%)$	47%	56%	30%
ε	0.38	N.A.	0.20

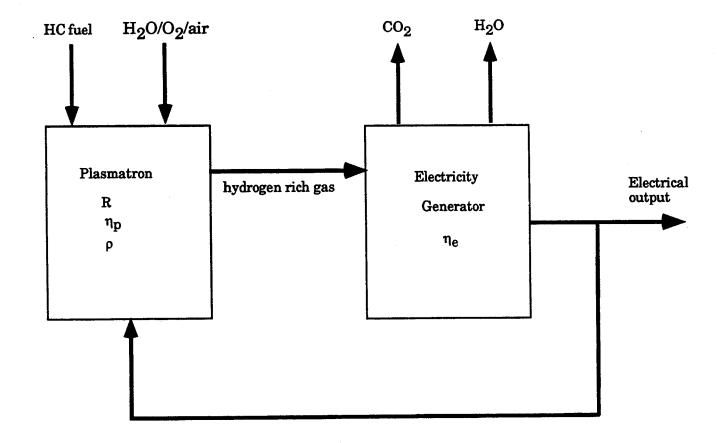
Table 4: Characteristics of CH_4 Plasma Reforming.

Net power output (kW)	1	10	100	1000
Plasmatron power requirement				
(no fuel cell) (kW)	0.55	5.52	55.2	552
Equivalent power input (kW)	2.13	21.3	213.	2130
Hydrocarbon fuel				
CH4 mass throughput (kg/hr)	0.138	1.38	13.8	138.
Reformate				
H_2 mass throughput (kg/hr)	0.045	0.455	4.55	45.5
CO mass throughput (kg/hr)	0.331	3.31	33.1	331.
H ₂ volume throughput $(10^{-3}m^3/s)$	0.141	1.41	14.1	141.

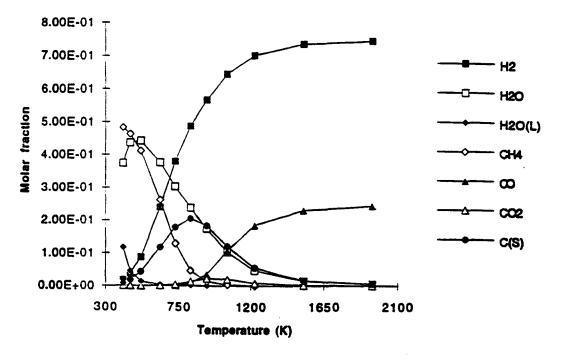
Table 5: Characteristics of CH₄ Plasma Steam-Reformer/Fuel Cell Systems.

Net power output (kW)	1	10	100	1000
Plasmatron power requirement				
(no fuel cell) (kW)	0.23	2.32	23.21	232.1
Equivalent power input (kW)	3.33	33.3	333.	3330
Hydrocarbon fuel				
CH4 mass throughput (kg/hr)	0.215	2.15	21.5	215
Reformate				
H_2 mass throughput (kg/hr)	0.054	0.539	5.39	53.9
C mass throughput (kg/hr)	0.161	1.61	16.1	161
H ₂ volume throughput $(10^{-3}m^3/s)$	0.168	1.68	16.8	168

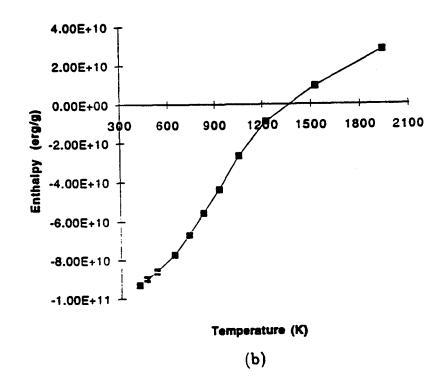
Table 6: Characteristics of CH₄ Plasma Thermal Decomposition/Fuel Cell Systems.



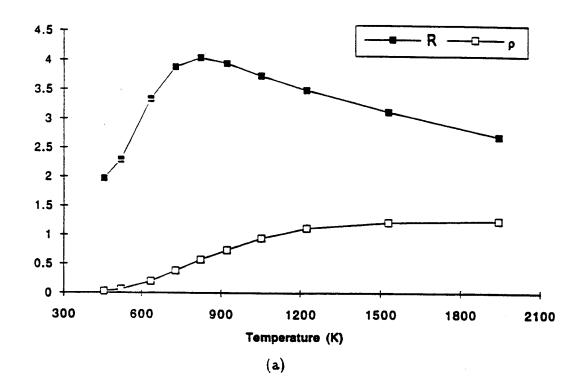




(a)







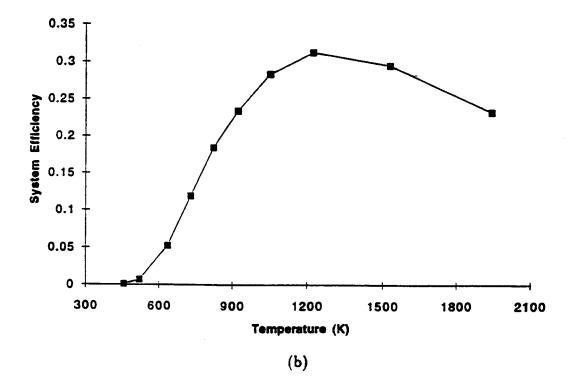


Figure 3

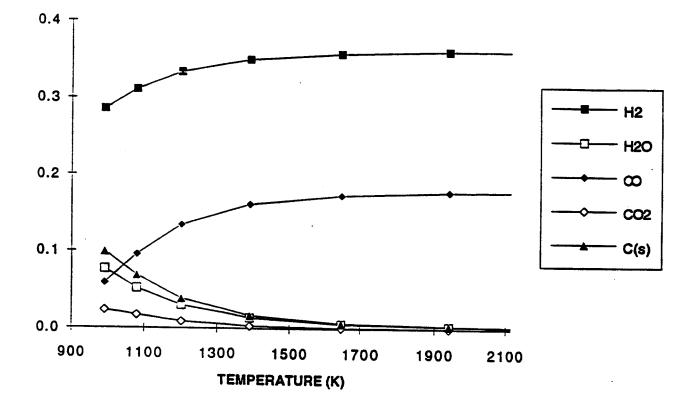


Figure 4

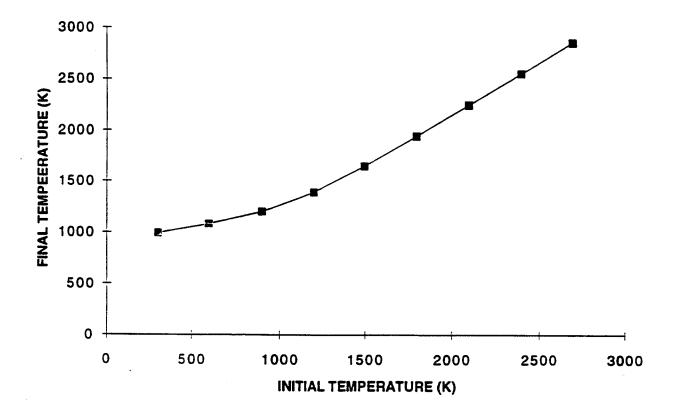


Figure 5

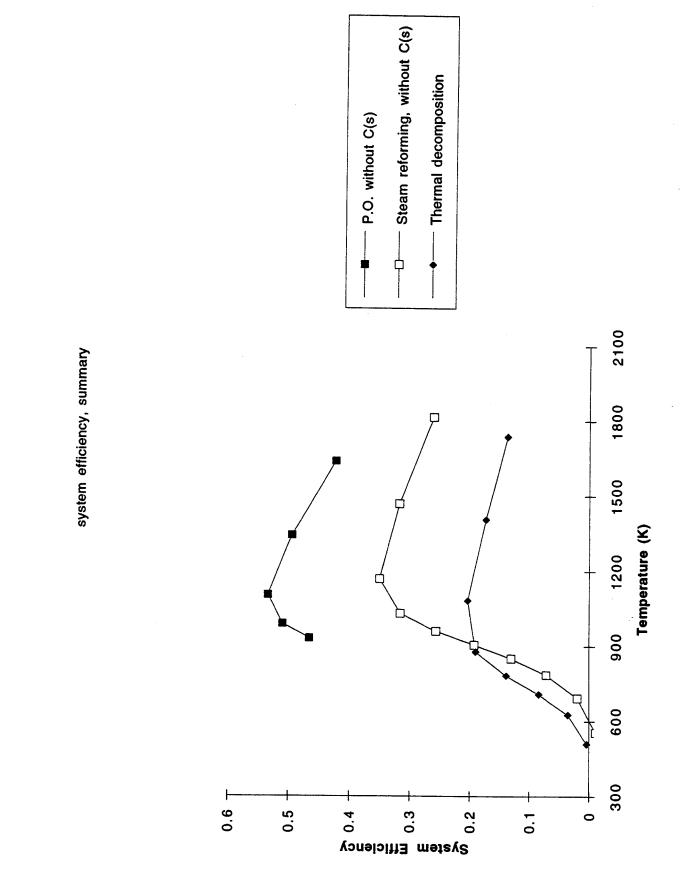


Figure 6

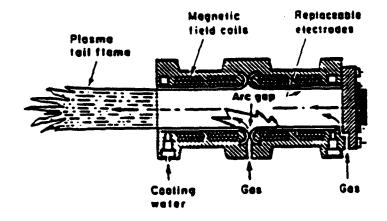
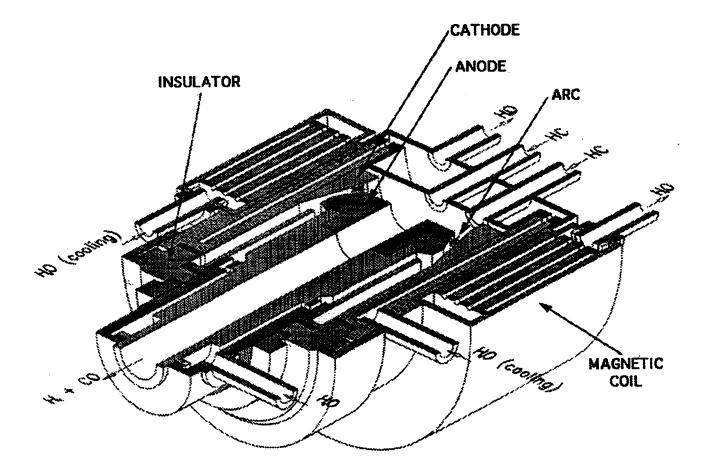


Figure 7



COMPACT PLASMA REFORMER



Figure Captions

Figure 1: Mass and energy flow diagram of a plasma reformer-fuel cell system

Figure 2: Results of high temperature steam reforming of methane. Constant pressure. (a) Molar fractions (b) Enthalpy

Figure 3: Results of high temperature steam reforming of methane at constant atmospheric pressure. (a) R and $\rho_{reformer}$ (b) η_s for $\eta_{fc} = 60\%$ and $\eta_{plasma} = 90\%$

Figure 4: Equilibrium molar fractions of partial oxidation reformate constituents as a function of the initial temperature of the air and methane

Figure 5: Final temperature as a function of the initial temperature of methane and air

Figure 6: Efficiency of a plasmastron/fuel cell system as a function of temperature, for methane, at constant pressure, with $\eta_{fc} = 0.6$ and $\eta = 0.9$, for several reforming technologies.

Figure 7: Westinghouse non-transferred AC/DC arc gas heater (from [Mac Rae]).

Figure 8: DC arc gas heater for plasma reforming of hydrocarbons

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