PLASMA CATALYTIC REFORMING OF NATURAL GAS

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Abstract

In this paper, recent results of plasma processing of natural gas are described. The use of a plasma reformer for the generation of hydrogen rich gas from natural gas has been investigated. In an accompanying paper, progress in plasma reforming of diesel fuel is described. The reformate composition has been investigated as a function of the initial mixture of air and methane. High methane conversion, near 100%, was obtained at relatively low values of plasmatron power. Soon-to-be-implements improvements in the overall reformer, including multiple heat exchanger for efficient thermal management and multiple water shift reactors, are described.

1. Introduction

Manufacturing of hydrogen from natural gas, biofuels and other hydrocarbons, is needed for a variety of applications. Plasma technology could provide important improvements in reforming hydrocarbon fuels for the production of hydrogen-rich gas for fuel cells and other applications [1-3]. The plasma conditions (high temperatures and a high 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:

- Economically attractive hydrogen generation with small production level
- high conversion efficiencies
- decreased problems of catalyst sensitivity and deterioration without soot production
- compactness and low weight (due to high power density) and minimal cost
- fast response time (fraction of a second)

Hydrogen-rich gas could be efficiently produced in compact plasma reformers from natural gas. The technology could be used to manufacture hydrogen for a variety of stationary applications (*e.g.,* distributed, low pollution electricity generation from fuel cells or hydrogen-refueling gas stations for fuel cell driven cars). It could also be used for mobile applications (e.g., on-board generation of hydrogen for fuel cell powered vehicles).

In this paper, the reforming of natural gas is investigated. The overall system is described in an accompanying paper [4] and will only be described briefly in section 2. The thermal management issues, not described elsewhere, are presented in section 3.

Experimental results from the kinetics investigation are described in section 4, for both the main reformers as well as for the water shift reactor. In section 5 the results are discussed and plans for future work are described. The conclusions are given in section 6.

2.   Experimental Setup

The plasmatron setup was similar to that described in the accompanying paper, and will not be described here.
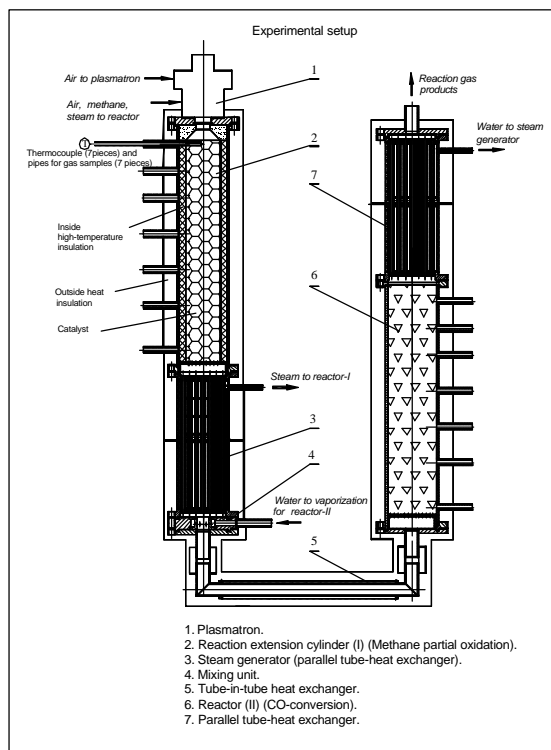

Figure 1. Experimental reactor for kinetic studies of methane partial oxidation by catalytic plasma reforming

In order to investigate the plasma catalytic process, an experimental reactor has been designed and built. It consists of reforming reactor and water-shift reactor. It has multiple sampling ports for both temperature and gas composition along the length of the reactor. The steel cylinders of both reactors have been thermally insulated with zirconia felt insulation, placed inside of the tubes. Multiple heat exchangers can be used, the first one after the reforming reactor and the second one after the water shift reactor.

A schematic of the setup is shown in Figure 1. The reforming reactor is placed directly downstream from the plasmatron and the mixing unit. This reactor is filled with a commercially available Ni-based steam reforming catalyst, crushed into 0.5 cm pieces. An air heat exchanger, in construction, will be placed downstream from the reforming reactor, to decrease the reformate temperature to that optimized for water shifting. The preheated air will be injected along side with the fuel into the mixing unit upstream from the reforming reactor.

The water shift reactor, downstream from the heat exchanger, is filled with Fe-based commercially available catalyst, crushed in the same manner as the steam reforming catalyst. A second heat exchanger is used to manufacture the steam required in the process.

3.   Thermal management, power losses and system efficiency

In this section, the thermal losses from the system are described and the exchangers designed for heat regeneration are described.

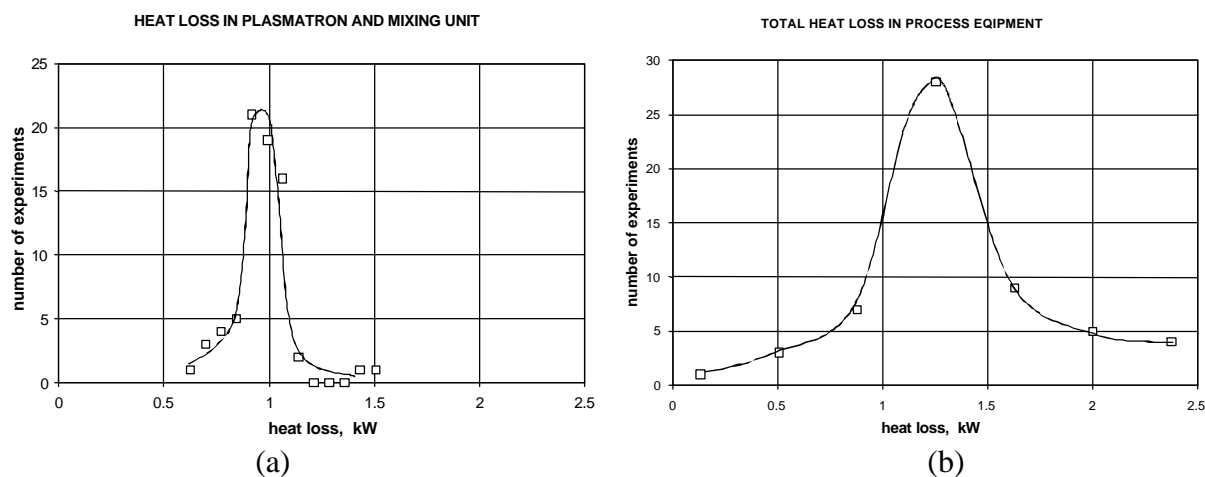(a)   (b)

Figure 2. (a) Histogram of losses in plasmatron/mixing unit; (b) histogram of losses in both plasmatron/mixing unit and reforming reactor.

With the novel reactor described in the accompanying paper, the temperature of the gas along the reactor has been measured. In addition to temperature measurements, the composition of the gas was also measured along the reactor using multiple sampling ports. The gas composition was analyzed using an HP M200D GC, with two columns and with two thermal conductivity detectors. The gas enthalpy is

determined from the gas temperature and composition. Decreased enthalpy of the gas as it flows downstream is due to losses in the system.

The losses in the plasmatron and the reforming reactor have been measured along the reactor, under many conditions of plasmatron operation and air/natural gas throughput. The plasmatron power was held approximately at 2.3 kW during these experiments. The results are summarized in Figure 2a, which shows a histogram of the energy loss in the section prior to the catalyst. The measured losses indicate that about half of the energy provided by the plasmatron has no effect on the reforming in the catalytic section. The typical loss is about 1 kW, with a relatively narrow distribution. The distribution of loss is due to noise in the measurements and due to the method of calculating the losses.

Figure 3. Counterflow heat exchanger

From the above discussion, it should be possible to decrease the plasmatron power by about a factor of 2 if the losses can be eliminated. Methods of eliminating the losses are described in Section 5.

The losses in the catalytic reactor are much smaller. A histogram of the losses in the plasmatron/mixing unit and in the reforming reactor is shown in Figure 2b. The average value of the combined losses is ~1.25 kW, vs ~1 kW in the plasmatron/mixing unit alone. Therefore, the losses in the reforming reactor are about 0.3 kW, not negligible but small.

An efficient gas-to-gas counterflow heat exchanger has been designed. In order to test the design, a version with reduced complexity was built and tested.. Figure 3 shows a picture of the device. The hot reformate flows through tubes, while the counterflowing air flows in-between tubes. The unit was built from steel for high temperature operation.

The reduced-complexity heat exchanger was tested and found suitable for operation with reformate gas. The heat recovery efficiency of the tested plasmatron was 20%, in agreement with calculations. The more efficient heat exchanger is in the process of being constructed.

4.   Kinetics of Catalytic Plasma Reforming

The experimental reactor was used to investigate the plasma catalysis process, with methane as the fuel.

A typical composition of the gas as it moves downstream in the reforming reactor is shown in Figure 4. For sufficiently high initial temperatures of the reagents, the process is complete about 10 cm into the reforming reactor, as shown in Figure 4(a). If the temperature is not sufficiently high, the conversion is incomplete even at the end of the reactor, as shown in Figure 4(b). It is possible to decrease the size of the catalyst reactor by increasing the temperature of the reagents. This can be done by preheating the reagents, or by increasing the plasmatron power.
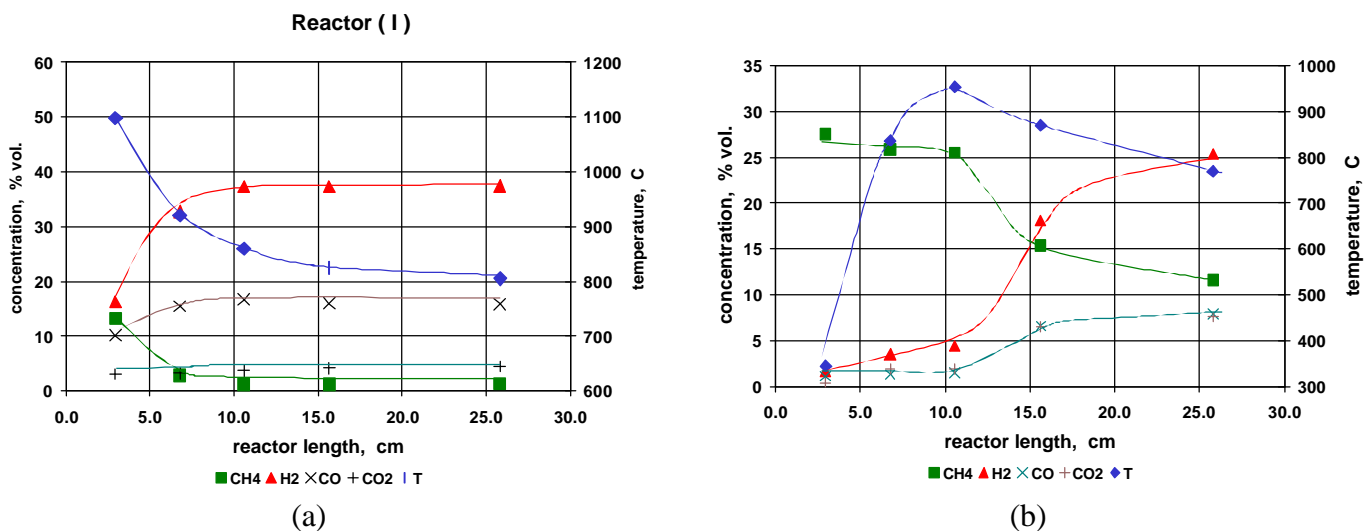

Figure 4. Reformate composition and temperature profiles along the reforming reactor for conditions of (a) complete conversion (b) incomplete conversion.

The water shift reactor performance is shown in Figure 5. It is clear that the water shift reactor was not sufficiently long for achieving the water-shifting reaction. The temperature is also shown in Figure 5 indicates that there are minimal losses in the water-shift reactor.

The best results obtained with the new system indicate a methane conversion of >95% with a specific energy consumption of 14 MJ/kg H_2, without the use of heat regeneration and with substantial thermal losses in the plasmatron/mixing unit. It is estimated that with reduced losses in the plasmatron/mixing unit and with the use of heat regeneration, it is possible to decrease the specific energy consumption to 7 MJ/kg H_2. At the lower specific energy consumption, the electrical requirements of the plasmatron are 5% of the heating value of the hydrogen generated.
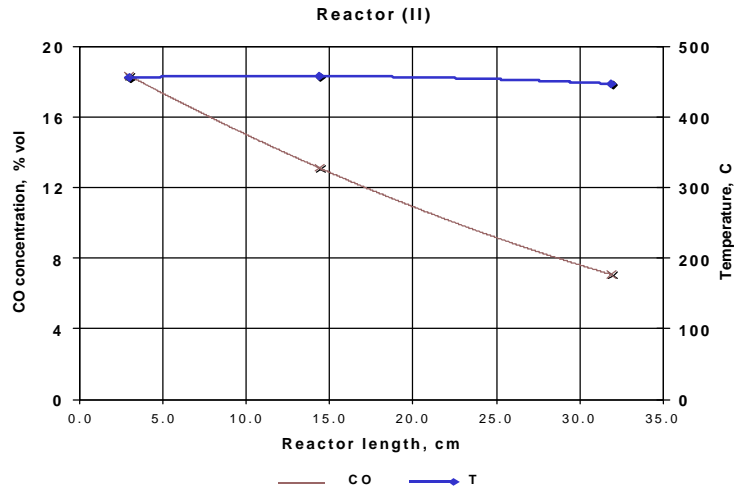
Figure 5. CO concentration profile in the water shift reactor.

The heat exchangers are under construction. The following section described methods of decreasing the large thermal losses in the plasmatron/mixing unit.
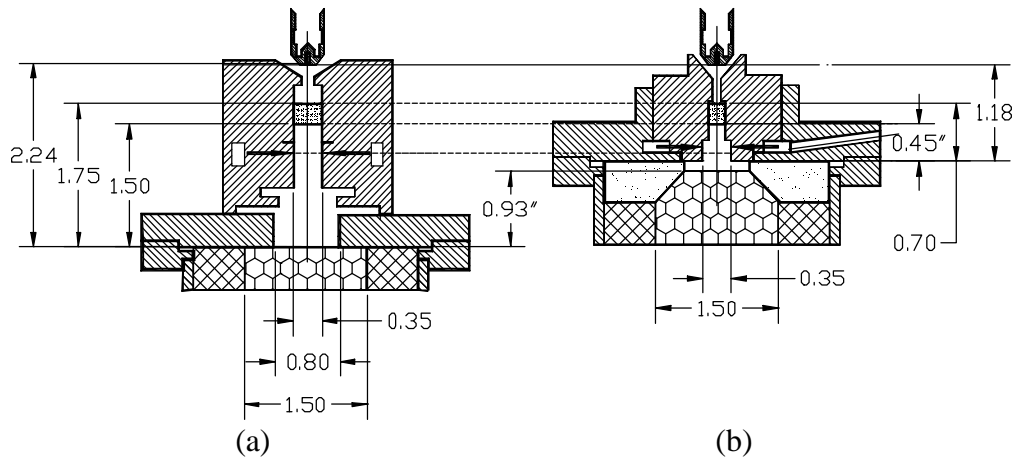

(a)   (b)

Figure 6. (a) Present plasmatron/mixing unit and (b) improved plasmatron/mixing unit

5.   Improved Thermal Management

As described above, the plasmatron and the mixing units have losses that amount to about ½ of the electrical input. The efficiency of typical plasmatron, without chemical processing, is on the order of 75-90%. The exothermic reaction that takes place in the mixing unit downstream from the plasmatron can increase the gas temperature and increase the losses. In this section, methods of minimizing the losses are described.

Figure 6(a) shows the plasmatron used in the experiments described in this paper. The mixing unit is an extension of the anode.   The anode is aggressively water cooled in order to minimize electrode erosion. Downstream from the mixing unit, a pair of water cooled flanges connect the plasmatron to the

reforming reactor. The thermal losses are due to the proximity of water cooled walls to regions of high temperature, increased because of the exothermic reactions that take place in the mixing unit. Although losses were expected, their magnitude was not.

In order to decrease the losses, it is necessary to redesign the mixing unit and the connection between the plasmatron and the reforming reactor. Figure 6(b) shows a schematic diagram of the modified setup. The mixing unit is shorter and flared, while the flange than connects the plasmatron to the reforming reactor is placed behind thermal insulation.

This setup should substantially decrease the losses. The unit shown in Figure 6(b) is being manufactured, and will be tested in the near future.

6.   Discussion

Two of the applications of the plasmatron reformers are decentralized hydrogen production applications (for hydrogen fueled vehicle fleets, for hydrogenation, and other) and for incorporation with a fuel cell stack for decentralized power production. Table I shows the characteristics of such systems, assuming a 3 kW fuel cell.

Table I

		Present Status	Near term goals	Long term goals
Decentralized hydrogen production application (natural gas)				
H2 production	g/s	1.7	1.7	1.7
H2 throughput	m3/hr	60	60	60
	cfm	30	30	30
H2 power	kW	200	200	200
Plasmatron electrical power	kW	20	10	5
Plasmatron power/H2 thermal power		10	20	40
Fraction of FC power to drive plasmatron		0.2	0.1	0.05
Decentralized fuel cells (diesel)				
H2 production	g/s	0.05	0.05	0.05
H2 throughput	m3/hr	1.80	1.80	1.80
	cfm	0.90	0.90	0.90
H2 power	kW	6000	6000	6000
Plasmatron electrical power	kW	0.94	0.47	0.24
Plasmatron power/H2 thermal power		6.36	12.73	25.45
Fraction of FC power to drive plasmatron		0.31	0.16	0.08
Fuel flexibility				

Three cases are shown in Table I. The first one refers to the presently achieved performance, with 14 MJ/kg H_2. The second one is for the near term extrapolation of 7 MJ/kg H_2, with decreased losses in the

plasmatron/mixing unit. And the last column is for a specific energy consumption of 3.5 MJ/kg H_2 achieved through efficient heat exchangers.

With methane at $2.5/MMBTU and with electricity at $0.05/kWhr, the presently achieved specific energy consumption indicates that the cost of electricity is about half that of the cost of the natural gas. This ratio is less than 1/3 for the near term and 1/5 for the long term.

Two groups are determining the cost of the hydrogen produced by a system that incorporates the plasma reforming: NREL [5] and a team consisting of MIT and BOC Gases (Murray Hill, NJ). These two groups are independently integrating a plasma reformer in a hydrogen manufacturing process, and evaluating the capital cost, the operating costs, and the cost of the hydrogen, as a function of plant capacity. These results will be presented in the near future at the American Chemical Society Symposium on Hydrogen Production, Storage and Use, New Orleans (August 1999) [6].

7.   Conclusions

The loss mechanisms in the plasma reformer have been determined through detailed investigation of the process using a new reformer and water-shift reactors. With this information a new plasmatron/mixing unit has been designed that will minimize these losses and substantially decrease the specific energy consumption of the plasmatron.

The reformer reactor kinetics have been studied. More knowledge is required in order to optimize the system. The optimization will yield smaller units and decreased cost of hydrogen. The same investigations in the water shift reactor indicate that the existing reactors length is inadequate at present, and longer units will be required for increased conversion of CO into H_2.

System that incorporate the plasma reformer have been scoped, and it has been determined that the cost of electricity is a small fraction of the final cost, even using present data.

Plasma catalytic reforming of natural gas offers the possibility of competitive production of hydrogen in small units.

Acknowledgement

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