USE OF A DIELECTRIC BARRIER DISCHARGE PLASMA REACTOR FOR HYDROGEN PRODUCTION

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SUMMARY

The use of atmospheric plasmas or cold plasmas reactors generated by dielectric barrier discharge (DBD) for chemical synthesis is currently being studied as an innovative technology. Due to its high reactivity, this technology can compete with thermal reforming processes for hydrogen production. In this paper, a DBD reactor in coaxial configuration is used to produce hydrogen from methane and water vapor mixtures. The reactor has a central electrode anodized to generate a thin oxide layer that serves as a second dielectric barrier that helps to increase catalytic sites. In the operation of the system makes use of diagnostic mechanisms that include optical spectroscopy and gas analysis by quadrupole residual gas analyzer with differential pumping, capable of measuring the input, output and exhaust gas recirculation system to determine the efficiency of production and selectivity to hydrogen.

1.- Introduction

Hydrogen is envisioned as one of the main energetic alternatives for mobile applications and low to medium power fixed applications; for such applications, the hydrogen is fed into a fuel cell that transforms the hydrogen into electricity [1]. The hydrogen to feed the fuel cell can be obtained typically via water electrolysis or hydrocarbon reforming. Both of these options reduce the efficiency of the system, since some of the electrical output of the system is used to either decompose the water or heat the system to the required temperature for the reforming reaction to proceed at an adequate rate. At the industrial level, hydrogen is produced from the steam reforming of natural gas, according to the following reaction [2]:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (1)$$

This reaction is highly endothermic, as evidenced by the strongly negative heat of reaction. In a commercial industrial hydrogen plant, about 1/3 of the gas consumption is devoted to increase and maintain the reforming reactor at temperature (800 – 900 ° C) [3]. Such energy and temperature requirements have to consequence of making profitable only large capacity plants, which translates into a "captive demand"; that is, the industrial hydrogen user satisfies its demand on site with a hydrogen plant. This scheme of concentrated production automatically requires infrastructure for transport and delivery to the end user, such as in the case of the natural gas market [4]. However, for the case of hydrogen, both technical and economical barriers have prevented the development of transport and retail infrastructure.

One of the main obstacles for a distributed production scenario is the energetic and economic efficiency of small-scale hydrocarbon reformers. There has been an important research effort devoted to the miniaturization of hydrocarbon reformers, which is challenging due to the severity of operating conditions, in particular for natural gas or typical hydrocarbon streams [5]. For mobile applications, the availability of an economic, small and safe hydrocarbon reformer would open the door for on-board reforming, a scheme where hydrogen would be generated in the vehicle using hydrocarbon fuel vapors as the source of hydrogen for the fuel cell.

The severity on reaction conditions, mainly pressure and temperature, is typically associated with thermodynamic equilibrium restrictions. In thermodynamic systems, the energy injection to the system is done via heat (to increase or maintain temperature) or mechanical work (to increase or maintain pressure). Electrical discharges are systems away from thermal equilibrium, since the free electrons in the medium can have temperatures thousands of times larger than that of the neutral atoms or molecules due to their high mobility when subjected to an electric field [6, 7]. These hot electrons can efficiently collide with the neutral gas producing excited molecules or even molecular fragments, which are much more reactive than the molecules on the ground state or those thermally excited [8]. In the present work, the utilization of dielectric barrier discharge reactors for the reforming of methane at low temperatures was explored.

The preliminary work presented here shows evidence of hydrogen production from methane at room temperature in a small prototype dielectric barrier discharge (DBD) reactor in the coaxial configuration, which has been observed previously by other authors [9-11]. Currently, a methodology for the quantification of hydrogen production using the available diagnostic tools is under development. Once this methodology is established, the evaluation of reaction conversion efficiency, the selectivity of the reaction system towards hydrogen and specific energy expenditure can all be evaluated by monitoring hydrogen production rate, methane consumption rate and electrical power input.

2.- Materials

The block diagram on Figure 1 shows the main elements of the experimental setup. These elements are discussed with detail in this section.

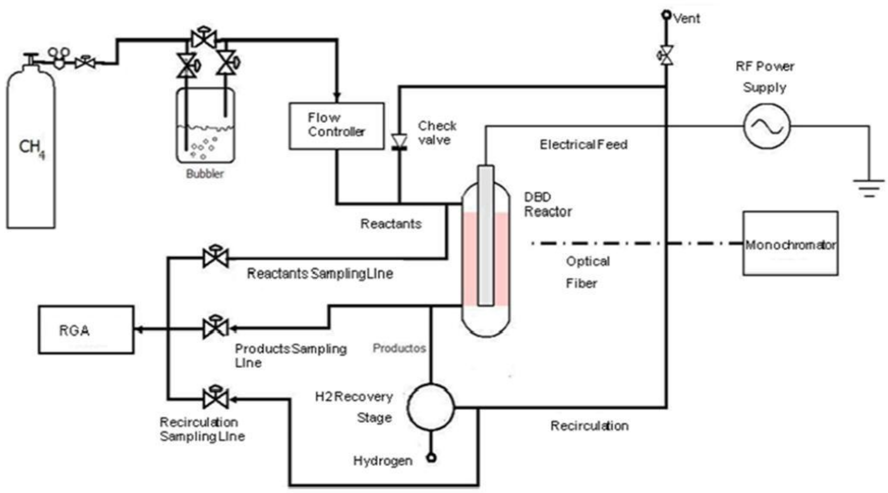

Figure 1. Block diagram of the experimental setup.

The gas feed system consists of a two-channel electronic mass flow meter, coupled to a proportional solenoid valve via a commercial PLC to establish a PID control loop, where the flow meter is the sensor and the solenoid valve is the actuator. This configuration was chosen because it gives maximum flexibility for the handling of gases, and also gives more freedom to choose hardware and to control the behavior of the gas streams. The system can inexpensively be expanded to 5 channels, and even more if a PLC with larger I/O capacity is chosen.

The electrical feed system is a half bridge inverter coupled to a resonant LC tank circuit that has been used previously to drive both DBD and arc discharges [12]. The role of the inverter is to generate the adequate frequency for the operation of the DBD reactor, typically in the range between 10 and 100 kHz. The inverter can be tuned to obtain the operating frequency that minimizes energy reflection. In the case of the resonant circuit, its function is to elevate the applied voltage to the level required, typically between 1 and 10 kV. Voltage amplification factors between 5 and 20 can be obtained with the present design. The output signal of the power supply is a sinusoidal signal with amplitude between 0 and 5 kV and frequency in the range 10 – 100 kHz.

The DBD reactor is a cylindrical quartz tube, with a 26 mm inner diameter and 1 mm wall thickness. The ends of the tube are sealed using two polyamide pieces with an o-ring groove. On the external surface of the tube, a metallic mesh is placed which serves as the grounded electrode. The top lid has an opening for an insulated electrical feedthrough, where an internal electrode 6 mm in diameter is attached; this internal electrode is the one subjected to the sinusoidal voltage supplied by the electrical feed system. To aid in the formation of a more homogeneous plasma, the internal electrode is anodized in an electrochemical cell to grow a thin (1 to 2 um) layer of aluminum oxide [13], which allows the operation in a double barrier configuration with the minimum energy dissipation.

For measurement of conversion, a differentially pumped residual gas analyzer (RGA) is used. The sampling is done via a very fine leak valve, which allows some of the gas to be sampled. In order to make quantitative measurements of conversion efficiency or specific energy expenditure, the signals obtained from the RGA have to be correlated to the entrance of the valve; the relationship between the partial pressure on the sampling line and the partial pressure measured by the RGA are related via the conductance of the leak valve and the pumping speed of particular species [14]. Currently, the procedure to correlate RGA signals with partial pressures on the sampling line is being developed by experimentally measuring the conductance of the leak valve for different gases and apertures and by the use of calibrated mixtures of gases.

3.- Results

The DBD reactor was fed with a mixture of Ar and CH_4 with a ratio 10:1 Ar/CH_4. The flow velocity was 2.0 liters per minute (lpm) for Ar and 0.2 lpm for CH_4. The gas streams were fed on independent lines and no extensive gas mixing was performed. The RGA spectrum of the reactor output when no electrical power was applied is shown in Figure 2. The reactor was then powered with a signal of 4 kV at 31 kHz, and the reactor output was sampled again with the RGA, resulting in the spectra shown in Figure 3.

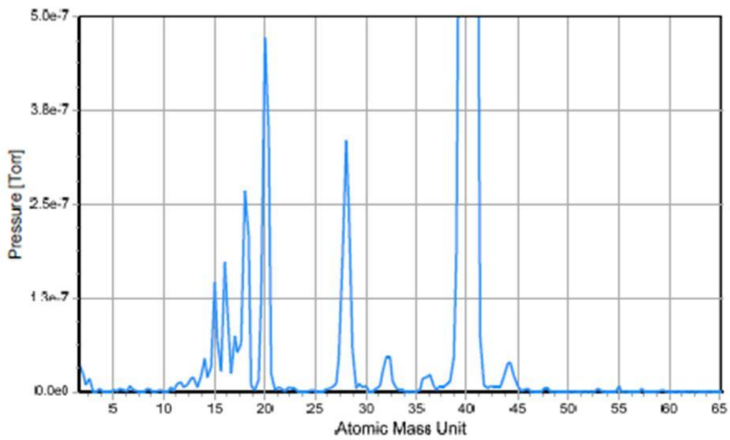

Figure 2. The RGA spectra of the reactor output when no electrical power was applied.

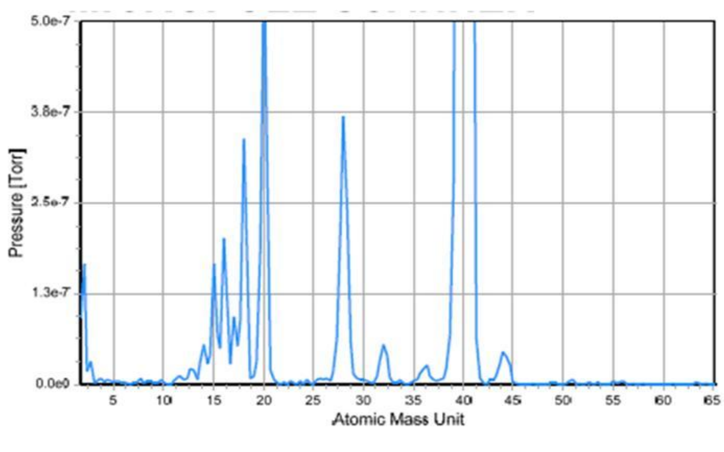

Figure 3. The RGA spectra of the reactor output when electrical power was applied.

The effect of the plasma operation can clearly be seen when the mass signal from Figure 2 is subtracted from the signal shown in Figure 3. This difference is plotted in Figure 4, where some features can be observed. First, an increase of the signal at mass 2, which corresponds to molecular hydrogen, is observed. Second, there is a slight decrease in the masses corresponding to CH_4 (masses 15 and 16), indicating some consumption of methane. Changes in mass 20 can be attributed to fluctuations in the argon flow, since it is large compared to the methane flow. Future experiments at lower Ar flows will help confirm this later hypothesis.

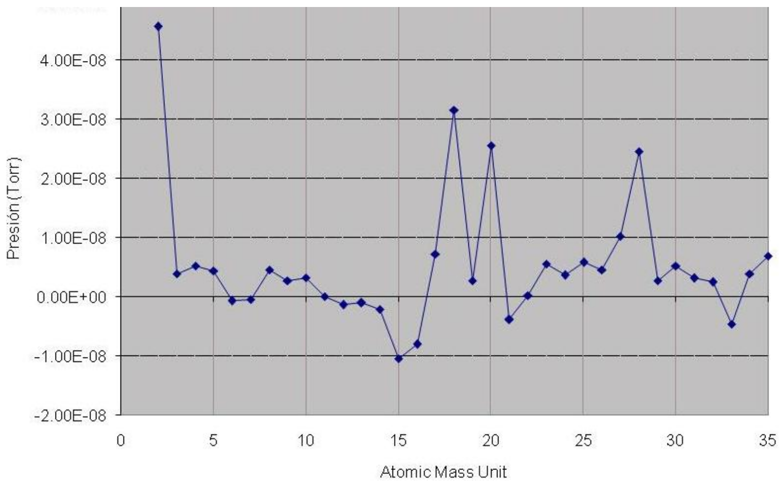

Figure 4. Difference between Figure 2 and Figure 3.

a)

b)

Figure 5. a) Discharge observed with Ar, b) Discharge observed with a mixture of Ar and CH_4.

Small additions of methane to the feed gas in the DBD reactor had a dramatic impact in operation when compared to pure inert gas. The color of the discharge changed from the pale blue observed with Ar discharge (Figure 5a) to the dark blue typically associated with methane flame (Figure 5b). The electrical characteristics of the discharge changed as well, requiring more input power and radiating much more electromagnetic noise, capable of even interfering with measuring devices such as oscilloscopes and the RGA electronic control unit. A small cylindrical Faraday cage has been built to surround the reactor and prevent this interference.

An indirect evidence of hydrocarbon decomposition was found after removing the central electrode for inspection. Spots of graphite-like material were found on the surface of the internal electrode, forming macroscopic tower-like structures. Since the only source of carbon into the system was the CH_4 gas, the presence of these structures can only be explained by the partial decomposition of methane on the plasma into carbon and hydrogen. The structures were primarily found near imperfections on the inner electrode (Figure 6a); inspection with a stereographic metallographic microscope reveal that the typical size is on the order of 1.0 mm long and about 200 um in diameter (Figure 6b).

a) *b)*

Figure 6. a) Carbon structures found near imperfections on the inner electrode, b) Structures inspected with a stereographic metallographic microscope.

The appearance of these structures on the electrode is detrimental for operation, since they tend to make the plasma channels concentrate on them and not cover the whole surface of the electrode, a fact that could lead to power dissipation problems for future industrial reactors of this type operating with much larger power levels. Operation with small amounts of CO_2 on the entrance has been shown by other authors to reduce the formation of soot particles on the reactor surfaces [15], an approach that will be explored further in future studies.

4.- Conclusion

Proof-of-principle experiments for the generation of hydrogen from methane have been performed on a coaxial dielectric barrier discharge reactor. With modest energy consumption and without requiring high temperatures or pressures, the reactor has demonstrated its capacity to extract hydrogen from methane gas. Two evidences that the process is taking place were found in this preliminary experiment: the detection of a mass 2 peak by the RGA monitoring the reactor output, indicative of the presence of hydrogen, and the formation of soot-like particulates in the internal surfaces of the reactor. Once a reliable technique to correlate RGA measurements with sampling gas composition is developed, the conversion efficiency and the specific energetic expenditure for the reactor will be calculated. Parametric studies with voltage, frequency and gas composition will be carried away to determine the optimal combination of operating parameters.

5.- Acknowledgements

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