THE PRODUCTION OF HYDROGEN FROM METHANE USING TUBULAR PLASMA REACTORS

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INTRODUCTION

There are many factors that are changing and shaping the fuel and energy industries of the future. Environmental, political, economic, and availability issues are just some of these factors. With environmental regulations becoming stricter, the emission of greenhouse gases is a major concern. With the decrease in oil resources, there is a need for other sources of fuel and chemical production.

Large quantities of hydrogen are used as a feedstock in the manufacturing of ammonia, methanol, and a variety of other petroleum processes. The synthesis of methanol occurs via the following reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH, \qquad \Delta H_{298} = -91 \text{ kJ mol}^{-1} \qquad [1]$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \qquad \Delta H_{298} = -50 \text{ kJ mol}^{-1} \qquad [2]$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \qquad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \qquad [3]$$

Synthesis gas (CO and H_2) production contributes a large fraction, approximately 60%, of the cost of methanol. The synthesis gas for methanol used to be manufactured by coke gasification, but now is almost exclusively produced by steam reforming of natural gas.

The production of hydrogen from methane has received a lot of research interest over the last decade. There are many good reasons for the conversion of methane, the principle component of natural gas, to other products. Natural gas is a very abundant resource with reserves throughout the world. Methane, with its 4:1 hydrogen to carbon ratio is also an excellent source for hydrogen. Hydrogen is projected to play an important role as a source of energy in the years to come. There will be a large increase in hydrogen demand as it becomes a general-purpose energy source for space heating, electrical power

generation, and as a transportation fuel (Balasubramanian, et al. 1999). Also, hydrogen is a clean burning fuel that can be stored as a liquid or a gas, and distributed by means of a pipeline (Armor 1999).

Catalytic steam reforming of methane is currently the primary means of hydrogen production. About 50% of all hydrogen produced worldwide is produced from methane, with 40% of that coming from the steam reforming of methane. It can be seen from Table 1 that the steam reforming of methane has the lowest CO_2 impact compared to other fossil fuels.

Table 1. Variance of CO_2 coproduction with different hydrocarbon feedstocks (Scholz 1993)

H_2/CO_2	Technology
4.0	Steam methane reforming
3.2	Steam pentane reforming
3.0	Partial oxidation of methane
1.7	Partial oxidation of heavy oil
1.0	Partial oxidation of coal

The production of hydrogen from steam methane reforming results from the following two reversible steps:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \qquad \Delta H_{298} = 206 \text{ kJ mol}^{-1} \qquad [4]$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \qquad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \qquad [5]$$

with the overall reaction written as follows:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2, \qquad \Delta H_{298} = 165 \text{ kJ mol}^{-1} \qquad [6]$$

While the reforming step [4] does not produce any carbon dioxide, it is the water gas shift reaction [5] that produces the carbon dioxide while removing the carbon monoxide and, in return, yielding another hydrogen molecule. Thermodynamically, the methane steam reforming process is favorable at high operating temperatures and low pressures due to the endothermic reaction and the increase in moles. The high operating temperature requires an intensive energy input to maintain these high temperatures. In addition, it is necessary to operate the system with excess steam in order to reduce the formation of carbon deposits. This in itself is an extra cost with the increase in equipment size.

Therefore, it is desirable to produce synthesis gas more economically. Cold plasmas or "non-equilibrium" plasmas have been shown to activate methane at temperatures as low as room temperature (Liu, et al. 1998). A cold plasma is characterized by high electron temperatures, while the bulk gas temperature can remain as low as room temperature, decreasing or eliminating the heat transfer energy requirements. It is the highly energetic electrons that allow for the conversion of methane that otherwise would not be feasible at these temperatures. In this paper, we discuss the use of our electrical discharge system to convert methane into hydrogen, acetylene, and carbon monoxide. A valuable feature of this system is the very low concentrations of carbon dioxide and water formed.

EXPERIMENTAL

In general, the experimental apparatus is similar to the system that has been described previously (Liu, et al. 1998). The feed gases consisted of a combination of methane, oxygen, hydrogen, and helium. Helium was only used in initial experiments and for characterization studies of the catalyst. The feed gas flowrates were controlled by Porter mass flow controllers, model 201. The feed gases flowed axially down the reactor tube. The reactor was a quartz tube with a 9.0 mm O.D. and an I.D. of either 4.5 mm or 7.0 mm. The configuration of the reactor can be seen in Figure 1.
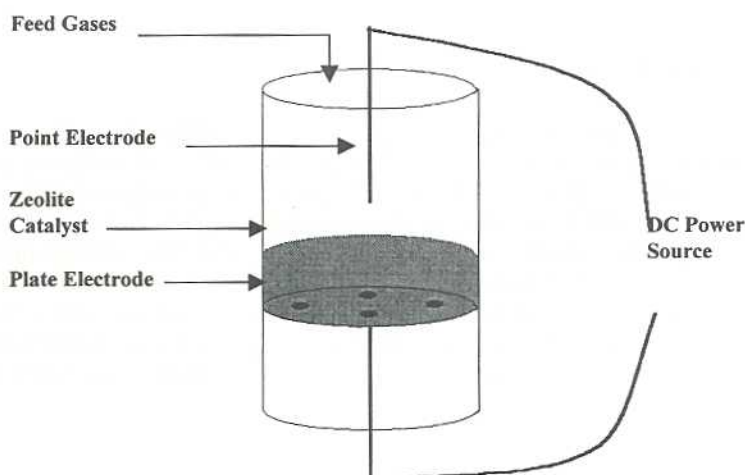
Figure 1. Point-plane dc reactor configuration with catalyst bed.

The reactor's electrode configuration consists of a point to plane geometry, meaning that the top electrode is a wire point electrode and the bottom electrode is a flat plate that also serves as a support for the catalyst. The top electrode is positioned concentrically within the reactor, and the gap between its tip and the plate is 8.0 mm. The catalyst is loaded from the top onto the flat plate electrode. A stainless steel wire cloth is placed between the electrode and catalyst in order to prevent the catalyst from falling through the holes on the electrode plate. Another stainless steel wire cloth is placed on top of the catalyst in order to prevent the movement of the catalyst. Due to the electrostatic nature of the zeolites and the plasma itself, this top screen is necessary to keep the catalyst bed uniform. The preparation and characterization of these zeolites has been discussed elsewhere (Liu, et al. 1996; Marafee, et al. 1997). The dc corona discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates Inc.).

As mentioned before, this system operates at low temperatures. A furnace around the reactor is used to heat the system to the desired temperature. The temperature is measured by an Omega K-type thermocouple that is attached to the outside of the reactor near the catalyst bed. The temperature measured on the outside has been calibrated against the internal temperature of the reactor, and has been discussed elsewhere (Liu, et al. 1996; Marafee, et al. 1997). However, when the operating temperature is below 373 K it is necessary to use cooling air to control the temperature since the plasma itself does heat the

gas to some extent. The system pressure varies depending on the experiment. The pressure is controlled using a GO back pressure regulator.

The product gases are passed through a dry ice/acetone bath that allows for any condensable organic liquids to be separated from the product gases. It should be noted that the dc system does not produce any liquids, including water. The effluent gases can be analyzed on-line by either a gas chromatograph or a mass spectrometer. The gas chromatograph is a CARLE series 400 AGC (EG&G) gas chromatograph equipped with a hydrogen transfer system to quantify the hydrogen; a HayeSep column to quantify carbon dioxide, ethane, ethylene, and acetylene; and a molecular sieve column to quantify oxygen, nitrogen, methane, and carbon monoxide. Also, a MKS mass spectrometer is used for on-line analysis of the products and for temperature programmed oxidation of carbon deposited on the catalyst.

RESULTS AND DISCUSSION

The plasma discharge, or cold plasma, is very effective in the conversion of methane at low temperatures. Figure 2 shows the effect of residence time on the conversion of methane. Reactors with two different cross sectional areas were employed to study bypassing of the feed gases around the plasma discharge because the streamer discharges only occupy a fraction of the reaction volume with the streamers moving around the plasma zone. The conditions in these two different reactors were identical except for the inside diameter of the reactors. The depth of the catalyst bed remained constant in both reactors; 0.1 grams and 0.04 grams were used in the large and small reactors, respectively. The original reactor had a 7.0 mm I.D., while the smaller reactor had a 4.5 mm I.D.
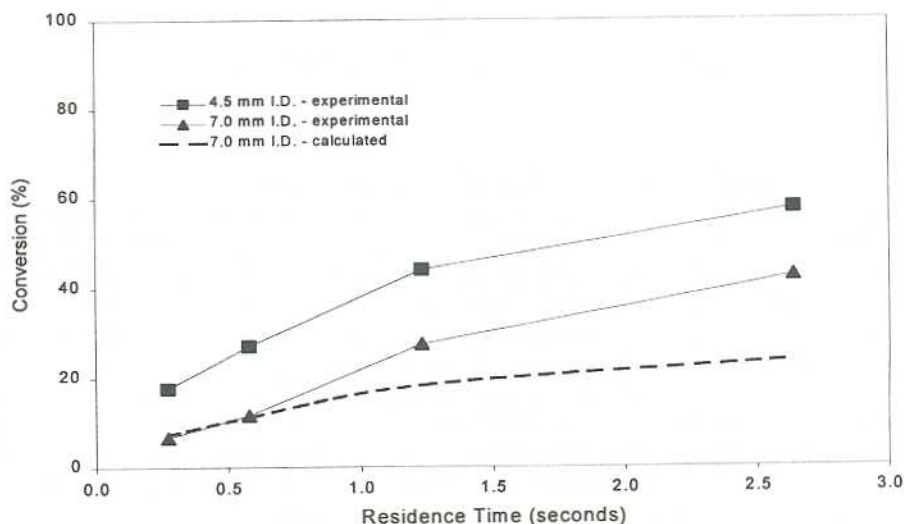

Figure 2. Methane conversion versus residence time in two different cross sectional area reactors. Feed composition, 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts. Calculated line is for 7.0 mm reactor based on 4.5 mm reactor data.

The fractional conversion is higher in the smaller cross sectional reactor for all residence times. As expected, the conversion increases as the residence time increases for both reactors. The data in Figure 2 show that the larger reactor has a lower conversion than

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the smaller reactor at the same residence time. This is indicative of bypassing, as the volume average rate of reaction is lower. This suggests that, in contrast to a typical homogenous reactor, there is a zone of higher reaction rate in proximity to the visible discharges and a zone of lower reaction rate, perhaps around the periphery of the reactor. However, if the added peripheral volume of the larger tube (from the difference between the cross sectional areas of the large and small tubes) were assumed to have no reaction, the dashed line drawn on Figure 2 would be expected. This is in agreement with the data at the shorter residence times, but the fact that the experimental data is higher at longer residence times suggests that some level of radial mixing occurs that reduces bypassing at lower velocities. As tube size is made larger such mixing would be desirable to increase the volumetric averaged reaction rate.

Hydrogen, acetylene, and carbon monoxide are the primary products of the conversion of methane in the dc plasma system. In addition, small amounts of ethane, ethylene, and carbon dioxide are produced. Of the C_2 products, acetylene accounts for 90%, while ethylene and ethane comprise 6% and 4%, respectively. Carbon dioxide is less than 0.2% of the effluent gas. No measurable amount of water is produced in the system.

The selectivity and yield of hydrogen, acetylene, and carbon monoxide can be seen in Figures 3-5. The definitions of conversion, selectivity, and yield for this system are as follows:

$$CH_4 \text{ conversion} = (\text{moles of } CH_4 \text{ consumed/moles of } CH_4 \text{ introduced}) \times 100\%$$

$$O_2 \text{ conversion} = (\text{moles of } O_2 \text{ consumed/moles of } O_2 \text{ introduced}) \times 100\%$$

$$\text{Selectivity of } C_2H_6 = 2 \times (\text{moles of } C_2H_6 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%$$

$$\text{Selectivity of } C_2H_4 = 2 \times (\text{moles of } C_2H_4 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%$$

$$\text{Selectivity of } C_2H_2 = 2 \times (\text{moles of } C_2H_2 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%$$

$$\text{Yield of } C_2 \text{ hydrocarbons} = CH_4 \text{ conversion} \times \Sigma(\text{selectivities of } C_2H_2, C_2H_4, C_2H_6)$$

$$\text{Selectivity of } H_2 = 0.5 \times (\text{moles of } H_2 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%$$

$$\text{Yield of } H_2 = CH_4 \text{ conversion} \times \text{selectivities of } H_2$$

$$\text{Selectivity of } CO = (\text{moles of } CO \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%$$

$$\text{Yield of } CO = CH_4 \text{ conversion} \times \text{selectivities of } CO$$

In general, the yields of the products follow the same trend as that of the methane conversion. The selectivities of the respective products did not vary much with either reactor size or residence time. Figure 3 shows that the selectivity of hydrogen has little variance between the different reactor sizes and residence times. The largest variance is 10%, with experimental uncertainty accounting for at least 2-3% of this.

The acetylene selectivity, seen in Figure 4, shows a trend of increased selectivity toward acetylene with residence time for both reactor geometries. In addition, the 4.5 mm reactor has a higher selectivity towards acetylene than the 7.0 mm reactor, and the difference in selectivity gets larger as residence time increases. Therefore, it seems that the higher the conversion, whether achieved by altering the reactor size or residence time, the

higher the selectivity towards acetylene. Carbon monoxide selectivity, shown in Figure 5, goes through a maximum at the intermediate residence times.

The above results were for a feed composition of 80% methane and 20% oxygen. In order to reduce carbon monoxide production impact, that might later have to be emitted as carbon dioxide, a study was done in which the feed composition was 66% hydrogen, 32% methane, and 2% oxygen (2/1 H_2/CH_4 with 2% oxygen). Previous studies showed that, with little or no oxygen in the feed, it is necessary to have a H_2/CH_4 ratio above one in order to achieve a stable plasma discharge in a non-oxidative environment. If the H_2/CH_4 ratio is less than one, the discharge will change from the streamer discharges to an unfavorable arc discharge. It is presumed that the 20% oxygen in the first set of experiments and the hydrogen in the second set of experiments play an important role in cleaning the catalyst, which in return plays an important role in the stability of the streamer discharges. It has also been determined from previous studies that 2-2.5% oxygen is still needed for the non-oxidative conditions. Concentrations lower than 2% have instability problems, while concentrations above 2.5% yield stable discharges, but do not increase methane conversion. In addition, the concentrations of oxygen above 2.5% do lower the selectivity towards C_2's and increase the selectivity towards carbon monoxide.

The effect of the feed composition on the fractional conversion is shown in Figure 6. The feed composition was the only parameter changed between the two systems. The fractional methane conversion is higher for the 2% oxygen system than the 20% oxygen system. However, the methane reaction rate, not shown, is higher for the 20% oxygen system due to the higher throughput of methane in the system. The conversion in both conditions increases with an increase in residence time.

Hydrogen, acetylene, and carbon monoxide are still the major products of both systems, while carbon dioxide is still very low and water is negligible for both systems. However, the selectivity of the major products is different in the two systems. Acetylene still comprises 90% of the C2's with ethylene and ethane around 6% and 4%, respectively.
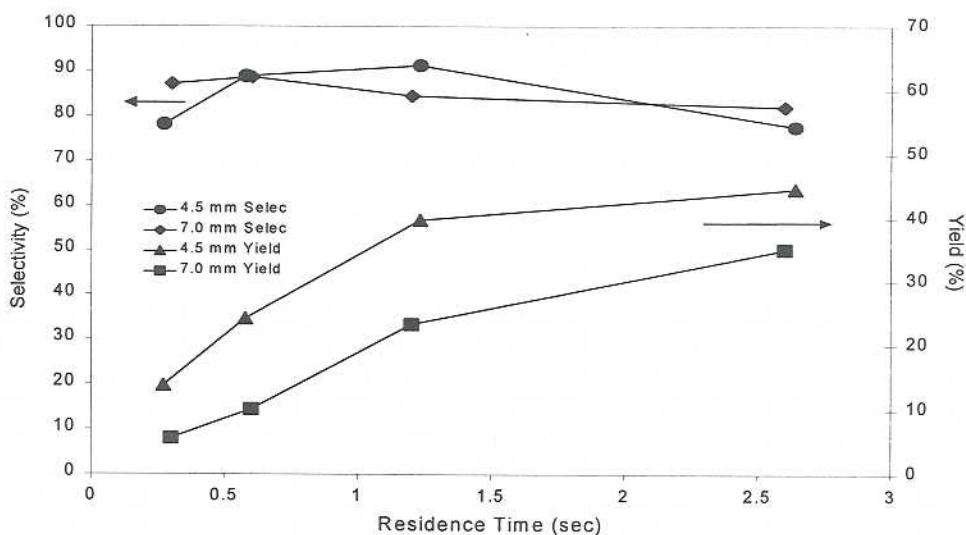

Figure 3. Hydrogen selectivity and yield for the two different reactor cross sectional areas at different residence times. Feed composition, 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.
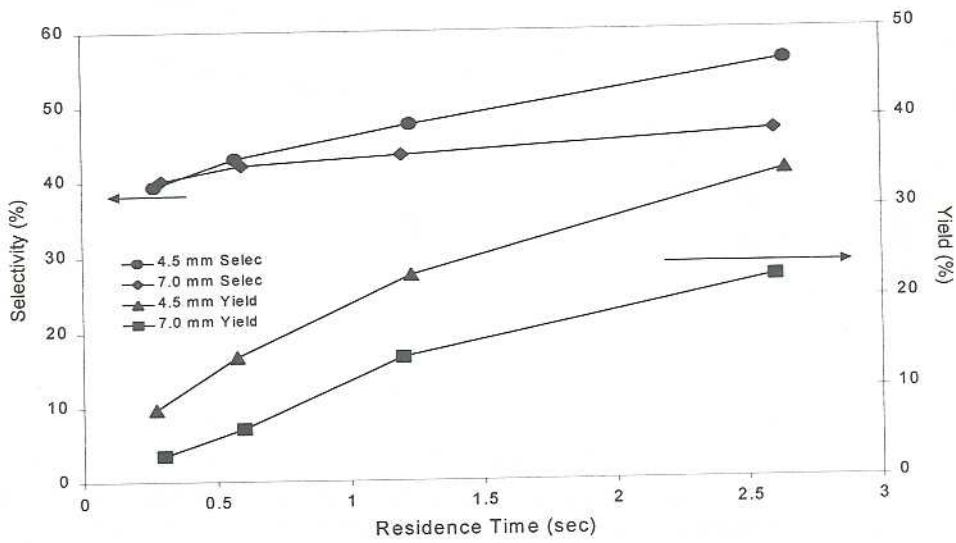
Figure 4. Acetylene selectivity and yield for the two different reactor cross sectional areas at different residence times. Feed composition, 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.
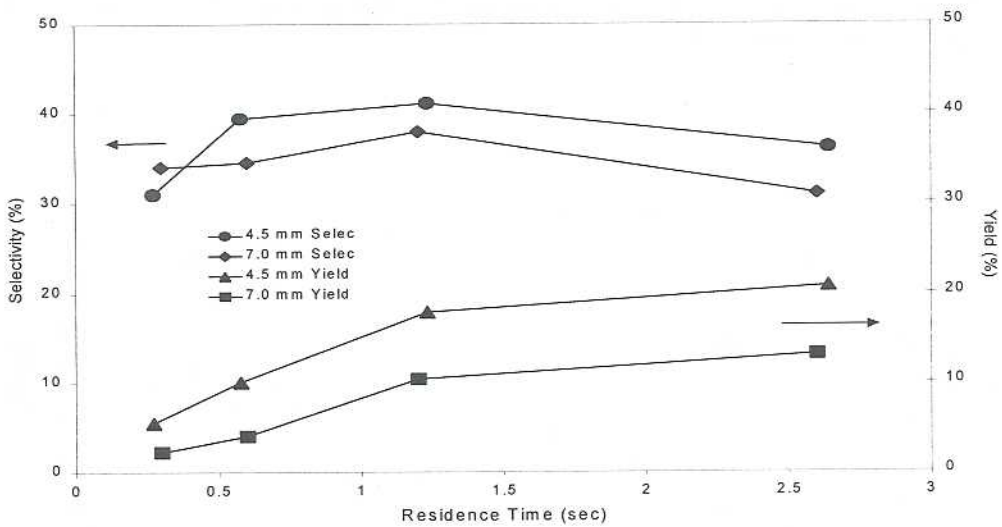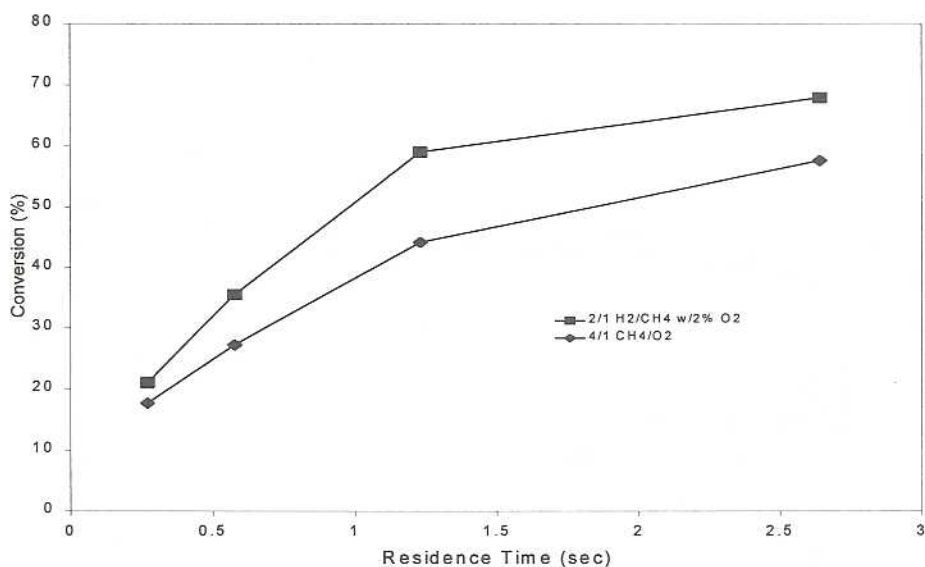

Figure 5. Carbon monoxide selectivity and yield for the two different reactor cross sectional areas at different residence times. Feed composition, 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.

Figure 6. Comparison of methane conversion versus residence time for two different systems: feed compositions of 2/1 H_2/CH_4 with 2% oxygen, and 4/1 CH_4/O_2. Gas temperature, 298 K; power, 5.2 watts.

Figures 7-9 show the effect of residence time on the selectivity and yield of the two different feed compositions. The yield basis for hydrogen includes only the net hydrogen produced from the reacted methane. The selectivity towards hydrogen, shown in Figure 7, is lower for the system that contains hydrogen in the feed. However, the conversion is higher in that system resulting in a hydrogen yield that is essentially the same in both systems at each residence time.
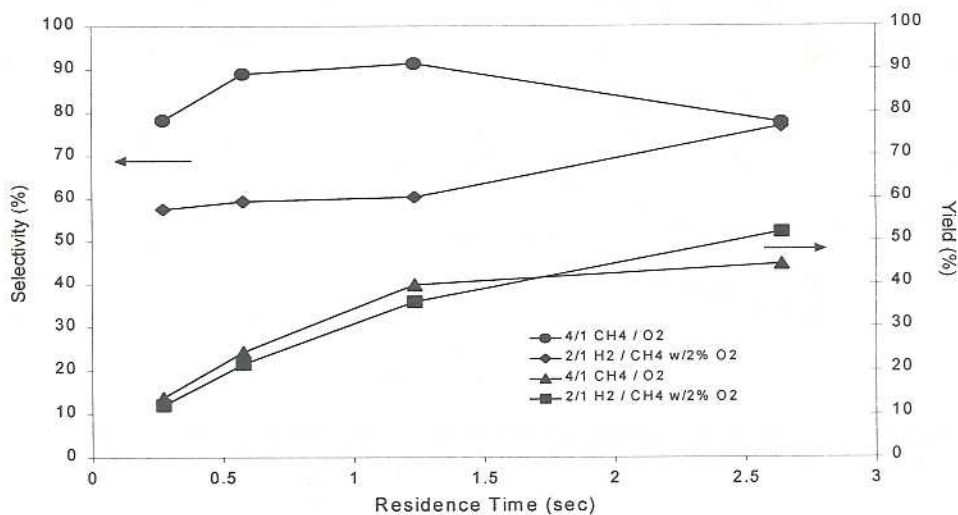

Figure 7. Hydrogen selectivity and yield for the two different feed compositions at different residence times. Feed compositions of 2/1 H_2/CH_4 with 2% oxygen or 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.
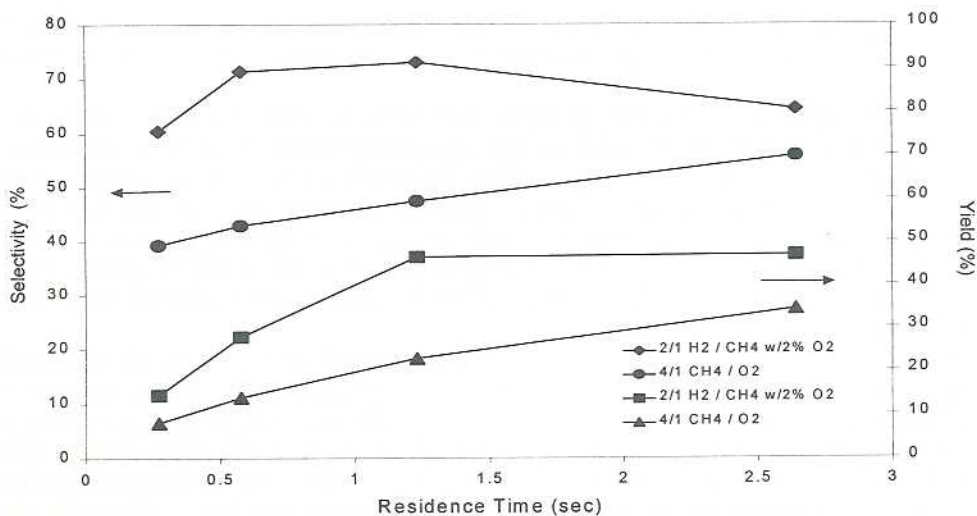
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Figure 8. Acetylene selectivity and yield for the two different feed compositions at different residence times. Feed compositions of 2/1 H_2/CH_4 with 2% oxygen or 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.
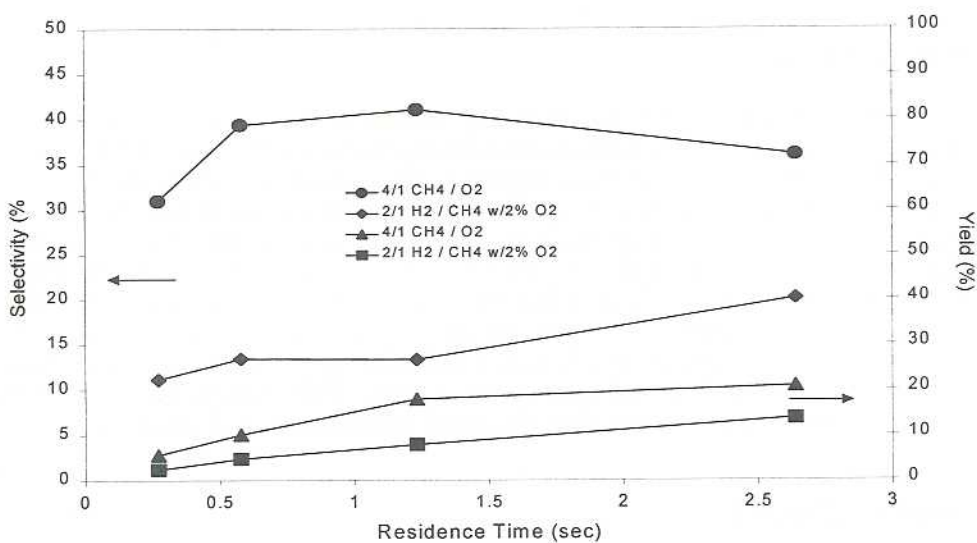

Figure 9. Carbon monoxide selectivity and yield for the two different feed compositions at different residence times. Feed compositions of 2/1 H_2/CH_4 with 2% oxygen or 4/1 CH_4/O_2; gas temperature, 298 K; power, 5.2 watts.

With the lower oxygen concentration, the 2% oxygen system shows a higher selectivity toward acetylene (Figure 8) and a lower selectivity toward carbon monoxide (Figure 9).

The high concentration of oxygen in the feed for the 20% oxygen system causes an over oxidation of the carbon species to CO, reducing the selectivity towards acetylene. This product flexibility could be useful in that it would allow for hydrogen to be produced

with acetylene for higher hydrocarbons or with carbon monoxide to produce a synthesis gas feed stream. Synthesis gas production is a very costly step in many industrial processes.

The production of hydrogen from methane is important because it has a low environmental impact. The production of hydrogen via steam reforming has a H_2/CO_2 ratio of 4 (Table 1), the lowest CO_2 impact of any fossil fuel source. The dc plasma system produces a H_2/CO_2 ratio of about 1000 in the effluent stream. However, CO is a major product of the system. If the water-gas shift reaction were used to convert all of the produced CO into CO_2 via reaction [5], the resulting H_2/CO_2 ratio would be approximately 9 for either system. This value is still considerably better than that of other fossil fuels, including steam reforming.

Hydrogen is not the only valuable resource produced in this system. As previously mentioned, the other by-products are acetylene and carbon monoxide. These products can return some value from either their heating or chemical value. The product gas stream of unreacted methane, acetylene, and carbon monoxide retains over 90% of the heating value that was put into the system via methane. However, the major cost of hydrogen production in this system is the energy required to obtain the plasma discharge. Currently, the production of hydrogen from methane in the catalytic dc system costs about four times the projected goal for the cost of hydrogen. However, the cost of hydrogen could be reduced if the acetylene was sold for its chemical value or even further processed to a higher value chemical.

CONCLUSIONS

The dc plasma catalytic system is very effective in the conversion of methane to hydrogen, acetylene, and carbon monoxide. Reducing the cross sectional area of the reactor decreased the amount of gas that was bypassing the streamer discharges resulting in an increase in methane conversion. Single pass methane conversions as high as 68% and hydrogen, acetylene, and carbon monoxide yields of 52%, 47%, and 21%, respectively, have been achieved. High hydrogen yields can be achieved under different conditions. The highest conversions were obtained with an oxygen concentration of 2% and a residence time of 2.6 seconds. Further work needs to be done to reduce the energy cost. The projected cost of hydrogen may be met by increasing conversion and the throughput of methane while maintaining similar power requirements. This could be accomplished by further minimizing bypassing to increase the overall efficiency of the plasma zone.

ACKNOWLEDGMENTS

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