

## Partial Oxidation of Methane to Form Synthesis Gas in a Tubular AC Plasma Reactor

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AC plasma discharges can produce valuable products, namely synthesis gas, from the partial oxidation of methane while maintaining low bulk gas temperatures. The products for this reaction are limited to synthesis gas, ethane, ethylene, acetylene, CO<sub>2</sub>, and water. The objective of the study is to maximize the partial oxidation of methane to synthesis gas and/or C<sub>2</sub> species using both pure O<sub>2</sub> and air and to minimize the electrical energy required for conversion.

### 1. INTRODUCTION

Many of the current and proposed methane conversion technologies involve the initial reforming or partial oxidation of methane to synthesis gas at high temperatures (> 700 °C). The synthesis gas may then be converted to methanol using a Cu/Zn catalyst or to higher hydrocarbons over an iron or cobalt catalyst via Fischer-Tropsch synthesis. These technologies are energy-intensive and are economically feasible only on a limited basis, typically on the largest possible scale. Nearly two-thirds of the cost is assumed in the production of synthesis gas. Lowering the expense of synthesis gas production is paramount to making methane conversion technologies more competitive particularly on smaller scales.

Considerable research has been focused on the use of electrical discharge plasmas to initiate many different chemical reactions. These studies include the conversion of methane to various products (Larkin 1998, Thanyanchotpaiboon 1998). Non-equilibrium electrical discharge plasmas are characterized by a large number of free electrons that are accelerated through a low-temperature gas by a large electric potential applied across a pair of electrodes. Normally, gases act as very good electrical insulators. If, however, an electric potential of sufficient strength is applied across the gas, free electrons within the gas are accelerated to high energies and can collide with the gas molecules resulting in ionization. Ionization produces more free electrons that are also accelerated and repeat the process until an electron "avalanche" occurs between the electrodes. The electron avalanche consists of high-energy electrons that produce a conductive path through the gas allowing electric charge to pass freely between the electrodes. This process is known as electric "breakdown."

The accelerated electrons can gain considerable energy in the electric field and are capable of transferring their kinetic energy to the molecules of the feed gas through inelastic collisions. These collisions can increase the internal energy of the gas molecules and may result in excitation, dissociation, or ionization without significantly increasing the bulk gas temperature. This increase in the internal energy of the gas molecules can overcome the

reaction activation energy allowing the species to be converted to various products. Since most of the energetic electrons required to activate the feed gas are located in a relatively narrow conduction channel, special consideration must be taken to design a reactor that will maximize the contact time between the energetic electrons and the neutral feed gas species.

Under the conditions of this study, the high energy electrons initiate chemistry that is predominantly free radical in nature and the energy transfer processes of the inelastic collisions do not involve significant heating. Thus the bulk gas temperature is not in equilibrium with the electrons and remains relatively low.

## 2. EXPERIMENTAL

This low-temperature plasma reactor consists of two electrodes, spaced axially, in a narrow quartz tube. The top electrode is a rounded point while the bottom electrode is a small flat disk (point-to-plane configuration). The feed gas flows axially from top to bottom through the discharge zone between the electrodes. The feed gas flow rates are controlled using Porter mass flow controllers. A Carle 400 Series gas chromatograph is used to analyze the composition of the exit gases. A soap bubble meter measures the exit gas flow rates.

An Elgar AC power system is supplied with wall current having a voltage of 120 V and a frequency of 60 Hz. Connected to the power supply is a multifunction generator that generates sinusoidal, square, or triangular waveforms and allows the frequency to be varied over the range used for these experiments. The output of the power supply is connected to a high voltage transformer. The high voltage cables from the transformer are connected to the electrodes of the reactor system. An Extech power analyzer that is connected to the low voltage side of the power circuit measures the voltage, frequency, current, power factor, and power consumed by the high voltage transformer and reactor system.

The *visible* discharge within the quartz tube appears as a small cluster of fine bluish filamentous "sparks" between the electrodes. These sparks, which are known as streamers, occupy a relatively small fraction of the total reactor volume. Some fraction of the feed gas bypasses these streamers and may not interact with the energetic electrons needed for activation. In order to decrease the feed gas bypassing the "active" reactor volume, the point electrode is forced to oscillate back and forth in a planar path parallel to the bottom electrode by means of an external magnetic field. The streamer discharges were observed to move through a larger fraction of the reaction zone as the point electrode oscillated. The electrical "efficiency" showed little improvement using this technique, but the formation of coke within the reactor became less problematic, resulting in a more stable discharge.

## 3. RESULTS AND DISCUSSION

The reaction of pure methane in the tubular AC plasma reactor under the conditions examined in this work is characterized by low conversions (< 5%) and poor electrical efficiencies (~100 eV/molecule CH<sub>4</sub> converted). The gaseous products are limited to C<sub>2</sub> hydrocarbons and hydrogen. It is apparent that the activation of the methane molecule in this environment is not very efficient. The presence of active oxygen species in the feed gas has been shown to considerably enhance the conversion of methane in dielectric barrier discharge plasmas (Larkin 1998). A base "standard" experiment in this study had a feed mixture of methane and oxygen at a 3:1 ratio flowing at 100 SCCM through a quartz tube with an inner

diameter of 7 mm. The gas gap between the electrodes was set at 1.0 cm. This resulted in a residence time of 0.231 seconds. The applied voltage was a sine wave with a frequency set at 300 Hz. The power for this experiment was fixed at 10 W.

The total methane conversion for this experiment was 24.4% and the oxygen conversion was 49.2%. These results show that active oxygen species greatly enhance the conversion of methane in this system as well. The methane conversion efficiency was determined to be 6.8 eV per molecule of methane converted. The addition of oxygen to the feed also changes the product distribution. 52.3% of the hydrogen from the reacted methane formed molecular hydrogen. The carbon-based selectivities were as follows: ethane (7.4%), ethylene (15.4%), acetylene (16.7%), carbon monoxide (40.0%), and carbon dioxide (5.2%).

A series of experiments was performed to study the effects of residence time. The reaction parameters were the same for the standard experiment, except the flow rate of the feed gas was varied between 400 and 20 SCCM giving feed gas residence times ranging from 0.057 to 1.128 seconds. The conversion and efficiency data are shown in Figure 1. Although the overall conversion of methane increases as the residence time increases, the reaction becomes less efficient. The overall rate of methane conversion is highest at low residence times. This suggests that the rate of methane conversion is a function of both methane and oxygen concentration. At low residence times, the methane conversion rate is higher because the methane and oxygen concentrations remain high throughout the entire reaction zone. As residence times increase and the overall conversion of methane and oxygen increases, the fractions of methane and oxygen become smaller, thereby reducing the average reaction rate of methane and lowering the overall efficiency of the reaction. The product selectivities also vary with residence time. As the residence increases, the selectivities of ethane, ethylene, CO, and CO<sub>2</sub> increase while acetylene decreases. The fraction of hydrogen produced changes little over the range tested.

### 3.1 Frequency, Waveform, and System Power

A series of experiments was performed to study the effect of changing the frequency of the applied voltage. All of the reactor parameters were held constant while the frequency was varied between 100 and 800 Hz. Varying the frequency of the voltage waveform caused the power factor and therefore the reaction power to vary as well. The applied voltage was adjusted for each frequency to maintain a constant power of 12 W. The total methane and oxygen conversion varied little for these experiments, suggesting that the total power consumption was the primary determinant for the extent of conversion. The selectivities of the gas products were also nearly the same for each frequency.

The next set of experiments tested how the shape of the voltage waveform might affect the reaction. Experiments used sine, square, and triangular voltage waveforms under the same reaction conditions. The results showed that the methane and oxygen conversions, as well as the product selectivities, were essentially the same for each waveform. The square waveform did, however, produce slightly more stable discharges at voltages just above breakdown.

Other experiments were performed to test the effect of increasing the system power from 10 W to as high as 30 W. At low power levels, both the methane and oxygen conversion increase linearly with power. At higher powers, the oxygen conversion increases to the point where the concentration of active oxygen species becomes limited. Thus, the increase in the methane conversion rate with increasing power becomes less pronounced since active oxygen is needed to enhance the reactivity of methane. The electrical efficiency decreases

with increasing system power because more and more energy is required to convert the available methane when active oxygen becomes depleted.

As the power applied to the reactor increases, the bulk gas temperature in the reaction zone increases. At higher temperatures, the thermal dehydrogenation reactions of methane to form olefins and carbon become more prevalent (Mallinson et al. 1992). The acetylene fraction increases considerably with system power. Excessive coking also becomes a problem at these higher power densities. The carbon deposits tend to form along the inner wall of the quartz tube or grow as fine filaments extending from the bottom electrode. Since this coke is electrically conductive, the current tends to flow almost entirely through these carbon deposits. This reduces the number of discharge streamers and limits the number of energetic electrons that can interact with the feed gases in the reaction zone, thereby lowering the conversion of methane in the reactor.

### 3.2 Pressure

Increasing the pressure within the reactor system is one way to increase the throughput of the feed gas without lowering the residence time. However, increasing the reactor pressure changes the electrical breakdown characteristics within the system. At higher pressure, the mean free path of free electrons accelerated in the applied electric field decreases. This means that the average electron energy is lower in the presence of the same electric field strength. A larger applied voltage is required to achieve electric breakdown and sustain the discharge under these conditions.

An experiment conducted at 2 atm was performed to examine the effect of increased reactor pressure on the conversion of methane and the distribution of products. A back-pressure regulator was used to set the reactor pressure at 15 psig. The methane-oxygen ratio remained at 3:1 while the feed gas flow rate was raised to 200 SCCM in order to maintain a residence time of 0.23 seconds. The minimum power required to obtain a stable discharge was higher at this pressure. The system power was fixed at 14 W. The other reaction conditions were the same as the standard experiment.

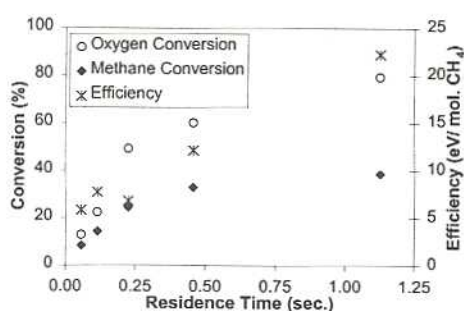
Although the high pressure experiment required more power to sustain a stable discharge, its electrical efficiency was better than the atmospheric pressure experiment. The overall methane conversions were similar for each experiment, 22.1% for the high pressure experiment vs. 24.4% for the standard experiment, but the larger throughput for the high pressure system resulted in an electrical efficiency of 5.6 eV/molecule of CH<sub>4</sub> converted vs. 6.8 eV for the standard experiment. The selectivities of several products differed for each system pressure as well. At higher pressure, the fraction of ethane produced was higher while ethylene and acetylene was lower. This was most likely due to the shift in the relative rates of the dehydrogenation-hydrogenation reactions at higher pressure to favor hydrogenated species. This also resulted in lower hydrogen selectivities at higher pressure as well, since more hydrogen is retained on the hydrocarbon products. The selectivities of CO<sub>x</sub> species did not change appreciably with changes in system pressure.

### 3.3 Pure Oxygen and Air

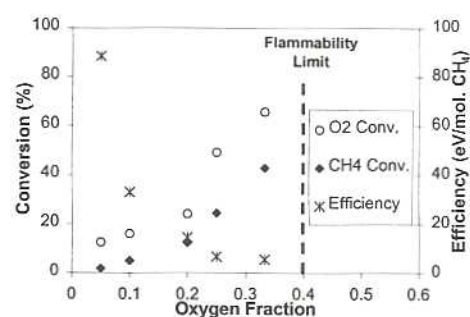
The next series of experiments was designed to examine how the concentration of oxygen in the feed affects the conversion of methane and the distribution of products. The methane - oxygen ratio was varied between 19:1 and 2:1, resulting in oxygen concentration that varied between 5% and 33% (maintained below the flammability limit). The other reactor

parameters were the same as the standard experiment. Figure 2 confirms that the addition of oxygen is effective at activating methane. The total methane conversion increases appreciably as the feed concentration of oxygen increases. The methane conversion increases from less than 2% with low oxygen concentration to nearly 45% at higher oxygen concentrations. This means that the methane conversion efficiency improves as well, decreasing from nearly 90 eV per molecule of methane converted at low oxygen fractions to under 6 eV at higher oxygen feed fractions.

Increasing the fraction of oxygen in the feed also changes the distribution of several major products. Figure 3 shows that the hydrogen selectivity does not change significantly for these experiments - remaining between 50% and 60%. But the selectivities of the  $\text{CO}_x$  compounds increase significantly as the concentration of oxygen in the feed increases. The carbon monoxide selectivity increases from 19% to 55% while the carbon dioxide selectivity increases from less than 1% to 6%. The  $\text{CO}/\text{CO}_2$  ratio remains high over this range of experiments because the activated oxygen is more likely to react with non-oxygenated species before completely oxidizing carbon monoxide.



**Figure 1** - Conversion and Efficiency vs. Residence Time for a Methane-Oxygen Feed ( $\text{CH}_4:\text{O}_2 = 3:1$ )



**Figure 2** - Conversion and Efficiency vs. Oxygen Fraction in the AC tubular reactor

The selectivity of ethane decreases rapidly as the oxygen concentration increases - from nearly 50% to under 4%. The selectivity of ethylene changes little at oxygen fractions below 20%, remaining between 14% and 18%, but drops to less than 10% as the oxygen fraction in the feed increases to 33%. The acetylene concentration increases rapidly as the oxygen fraction increases from 5% to 10%, but remains relatively constant as the oxygen fraction is raised further. The increase in olefin production at higher oxygen concentrations may be due to an increase in the reactor temperature from exothermic oxidative reactions. The higher temperatures increase the likelihood of dehydrogenation reactions. The slight decrease in the  $\text{C}_2$  selectivities at the highest oxygen fractions can be attributed to a significant increase in the relative rates of oxidation reactions.

Using pure oxygen in large quantities can be of prohibitive cost, especially for smaller operations. Since air separation to provide pure  $\text{O}_2$  is a significant expense, the use of air for the partial oxidation of methane would appear to be an interesting alternative. Experiments were performed to show how the partial oxidation of methane using air compares to that of using pure  $\text{O}_2$ . Since the best methane-oxygen results were at a methane-oxygen ratio of 2:1, the feed gas used for the methane-air experiments was a combination of 71% air and 29%

methane, resulting in a methane to oxygen ratio of 2:1. This meant that a majority (~56%) of the feed gas was nitrogen. Nitrogen does not react very readily in the discharge environment, so it acts primarily as a diluent and a heat sink for the reaction. A higher system power of 16 W was used for these experiments. The nitrogen absorbed some of the heat generated by the exothermic partial oxidation reactions, making excessive coking less of a problem. Feed gas flow rates were varied between 100 and 800 SCCM. Higher flow rates were used in order to obtain similar methane throughputs as previous residence time experiments. The other reaction parameters were the same as the standard experiment.

Figure 4 shows the methane and oxygen conversion and the conversion efficiency for the methane-air system at the different residence times. Relatively high methane and oxygen conversions were obtained despite the large nitrogen dilution. Since conversions were high, the electrical efficiencies remained reasonably low, being only slightly higher than those obtained for the pure O<sub>2</sub> system. A qualitative analysis to determine the presence of NO<sub>x</sub> compounds found that NO<sub>2</sub> was present in the product stream, NO levels were on the order of about 10 ppm, and N<sub>2</sub>O was below detectable levels.

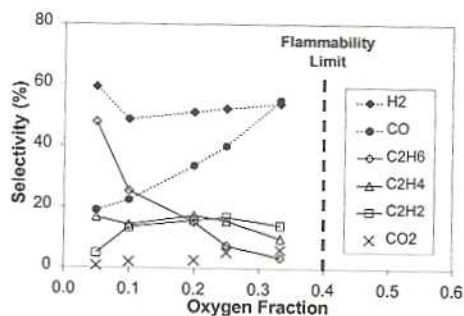


Figure 3 - Product Selectivity vs. Oxygen Fraction in the AC tubular reactor

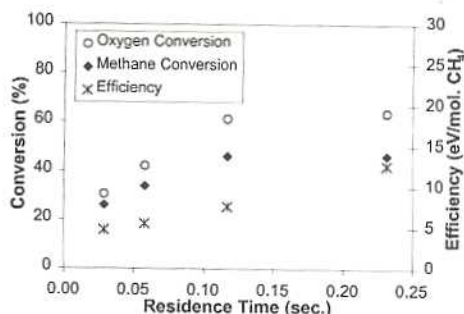


Figure 4 - Conversion and Efficiency vs. Residence Time for a Methane-Air feed (CH<sub>4</sub>:O<sub>2</sub> = 2:1)

#### 4. CONCLUSIONS

A range of reaction parameters has been varied to study their effects on methane conversion, product selectivity, and energy consumption in the AC tubular reactor. The results indicate that increasing the oxygen fraction in the feed enhances the activation of methane in the reaction. Also, reducing feed gas bypassing, operating at low power, and increasing the reaction pressure all improve the efficiency of methane conversion.

#### ACKNOWLEDGEMENTS

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