ENHANCEMENT OF METHANE CONVERSION
USING ELECTRIC FIELDS

FINAL TECHNICAL REPORT

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Executive Summary

The goal of this project is the development of novel, economical processes for the conversion of natural gas to more valuable products such as synthesis gas or direct conversion to methanol, ethylene and other organic oxygenates or higher hydrocarbons. The methodologies of the project are to investigate and develop low temperature electric discharges and electric discharge-enhanced catalysis for carrying out these conversions. With the electric discharge-enhanced conversion, the operating temperatures are expected to be below those currently required for such processes as oxidative coupling, thereby allowing for a higher degree of catalytic selectivity while maintaining high activity.

In the case of low temperature discharges, the conversion is carried out at ambient temperature, trading high temperature thermal energy for electric energy as the driving force for conversion. The low operating temperatures remove thermodynamic constraints on the product distribution due to the non-equilibrium nature of the low temperature plasma. This also removes the requirements of large thermal masses that need very large-scale operation to maximize efficiency that is the characteristic of current technologies, including high temperature plasma processes. This potentially allows much smaller scale processes to be economical. Additionally, a gas conversion process that is electrically driven provides an internal use for excess power generated by proposed Fischer Tropsch gas-to-liquids processes and can increase their internal thermal efficiency and reduce capital costs.

This project has studied several different types of low temperature plasma reactors and operating conditions. These include AC and DC tubular non-dielectric reactors, with the DC system using a catalyst. In AC barrier discharge reactors, we have studied both partial oxidation and direct formation of higher hydrocarbons in a pure hydrocarbon environment.

The best results for energy use with high methane conversions have been found in the tubular (non-dielectric) reactors at residence times from tenths to a few seconds. The primary products under these conditions are C_2 hydrocarbons or C_2 plus synthesis gas. Energy use appears to be below those of conventional (thermal-catalytic) processes in some cases, but where it is higher, other advantages of these systems may allow an economic and efficient process to be developed. Partial oxidation to form liquid oxygenates appears to be feasible in dielectric barrier reactors with higher energy consumption and longer residence times. Pressures up to three atmospheres have been found to be advantageous.

The tubular catalytic dc reactor system has shown to be an effective method in the conversion of methane at room temperatures while maintaining high selectivities. This system has been found to be effective at low temperature using a zeolite catalyst system that stabilizes the discharge and enhances conversion and selectivities. The system can produce high selectivities of C_2 hydrocarbons, hydrogen, and synthesis gas. The product distribution can be controlled by operating in a non-oxidative environment (methane plus hydrogen) to produce C_2 hydrocarbons and hydrogen, or in an oxidative environment

(methane and oxygen) to yield synthesis gas and a lesser amount of C_2 's. Another valuable feature of this system is the very low concentrations of carbon dioxide and water formed, even under the oxidative conditions. For the non-oxidative system, conversions are as high as 70% at residence time of 2.6 seconds, while maintaining acetylene, hydrogen, and carbon monoxide selectivities of 65%, 75%, and 20%, respectively. Methane conversion for the oxidative system is 55% at a similar residence time with selectivities for acetylene, hydrogen, and carbon monoxide are 55%, 75%, and 40%, respectively. Control of C_2 product distribution has been shown to be achievable with the addition of metallic components to the catalyst.

Experiments using a low temperature AC discharge within a quartz tube reactor were initiated in an attempt to directly form more valuable products from the partial oxidation of methane. Oxygen is included in the methane feed to increase the activation rate of methane. The primary products for this particular reaction are hydrogen, CO, acetylene, ethylene, and lesser amounts of ethane, CO_2 , and water. The best results have come using a feed mixture of methane and oxygen at a 2:1 ratio and a residence time of 0.05 seconds. The methane conversion was 50 percent resulting in a gross energy consumption of about 3 eV per molecule of CH_4 converted. These are the best results among all of our systems and are lower than net energy use for conventional catalytic systems. Higher conversions are achieved at modestly longer residence times.

We have used a silent electric discharge (SED) reactor (also known as a dielectric barrier discharge (DBD) reactor) to generate a non-equilibrium plasma for the direct partial oxidation of methane to methanol at ambient temperature and atmospheric pressure. The primary products are organic oxygenates (methanol, formaldehyde, methyl formate and formic acid), hydrogen, carbon monoxide, carbon dioxide and water. We have achieved a better understanding of the role of oxygen in the process, manipulated process parameters to enhance the oxygenate yield and energy efficiency while minimizing the CO_x yield, and gained further insight into the reaction pathways that are present in this system. Methane conversions over 50 percent, organic oxygenate selectivities above 60 percent and production of a CO_2/CO and hydrogen syn gas have been achieved. In addition, the water-gas shift and reverse-water gas shift reaction pathways have been shown to exist in the system. Higher methane conversions to organic liquid oxygenates with increased energy efficiency can be obtained by using reactors in series with intermediate oxygen additions. We have shown that operating at lower temperature within the reaction zone increases the fraction of organic oxygenates that condense within the reactor, therefore enhancing their yield by avoiding over-oxidation. Using a methane/oxygen-enriched-air mixture suggests nitrogen acts only as a diluent and does not affect the chemistry. Our best result for partial oxidation thus far has been 46 eV per molecule of methane converted.

The silent electric discharge reactor has also been found to be capable of converting over 50% of a methane feed to higher hydrocarbons. The most efficient pure methane reactions in the SED reactor have been in the 6.35 mm gas gap reactor using relatively low residence times (< one minute). The best conversion efficiencies for this system have been about 150 eV/molecule CH_4 reacted, but the per pass conversions for these

results were less than 5%. However, energy consumption is presently too high and the residence times are too long to develop an industrially feasible process based on the current reactor design parameters.

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INTRODUCTION

This report summarizes the conditions and results of this multifaceted program. Detailed experimental descriptions and results and discussion can be found in the publications cited in the Appendix. The goal of this project is the development of novel, economical, processes for the conversion of natural gas to more valuable projects such as synthesis gas or direct conversion to methanol, ethylene and other organic oxygenates or higher hydrocarbons. The methodologies of the project are to investigate and develop low temperature electric discharges and electric discharge-enhanced catalysis for carrying out these conversions. With the electric discharge-enhanced conversion, the operating temperatures are expected to be far below those currently required for such processes as oxidative coupling, thereby allowing for a higher degree of catalytic selectivity while maintaining high activity.

In the case of low temperature discharges, the conversion is carried out at ambient temperature, trading high temperature thermal energy for electric energy as the driving force for conversion. The low operating temperatures remove thermodynamic constraints on the product distribution due to the non-equilibrium nature of the low temperature plasma. This also removes the requirements of large thermal masses that need very large-scale operation to maximize efficiency that is the characteristic of current technologies, including high temperature plasma processes. This potentially allows much smaller scale processes to be efficient. Additionally, a gas conversion process that is electrically driven provides an internal use for excess power generated by proposed Fischer Tropsch gas-to-liquids processes and can increase their internal thermal efficiency and reduce capital costs.

This project has studied three primary types of low temperature plasma reactor and operating conditions. The organization of this program is shown schematically on the next page. Typical small scale laboratory reactor systems were developed that used mass flow controllers for feed gas mixture delivery and GC and MS analysis of products. The range of operation included flow rates from a few sccm to a few hundred sccm with residence times from less than a tenth of a second to about 30 minutes. Temperatures used were generally from ambient to 100 °C, but were from as low as about 0 to a high of about 800 °C. Pressures were generally atmospheric, but for most of the configurations pressures up to 3 atmospheres were also used.

AC dielectric barrier discharge (DBD) reactors, also known as silent electric discharges (SED) originate from the design of ozone production reactors. In these reactors the reacting gas flows between two electrodes, with one electrode (in this project) covered by a glass dielectric. Annular and planar reactors have been used. The origin of this project was the study of methane partial oxidation in an annular ozone-type reactor. Also in the annular reactor, we studied the production of higher hydrocarbons from pure methane and hydrocarbon mixtures in order to determine process feasibility and also to understand changes in the behavior of reactions due to reactor design and operating variables.

The AC non-dielectric studies have focused almost entirely on non-catalytic partial oxidation operation. Catalysts used in the DC system have, thus far, promoted more combustion reactions under the partial oxidation conditions that have been used.

AC Power for both the dielectric and non-dielectric reactor systems was provided by means of an AC power supply with waveform generator. This output was stepped up

using transformers. Power was always measured on the low voltage side and therefore included losses in the step up transformer and the reactor itself.

The non-dielectric reactors, for both AC and DC operation, consist of a quartz tube with axially placed upper and lower electrodes. Although a number of different electrodes have been used, most of the results were obtained using a plate lower electrode (a disc with holes for gas to pass through) with an upper wire electrode mounted concentrically. When catalysts have been used, a wire cloth screen is placed on the lower electrode to retain the catalyst.

DC operation, using only non-dielectric reactors, has almost always been with a catalyst. Without a catalyst, the discharge is not stable except at fairly high temperatures, where thermal plasma conditions appear to occur and coking takes place. The properties of the catalyst are quite important, but our knowledge of their specific roles remains very limited as the applied objectives of this project limited our ability to study fundamentals. Although numerous catalysts were tried, including many mixed oxides designed for catalytic oxidative coupling, the best have been zeolites. This may be due to the electrostatic properties of the zeolite cage as well as the types of surface sites. Acidic zeolites promoted substantial coking. This work focused on non-oxidative coupling of methane to form C_2 . The feed gas needed substantial hydrogen and a small amount of oxygen in order to have stable operation. The primary C_2 product was acetylene. In the last stages of the project, metallic elements were added to the zeolites. These "promoted" catalysts were found to cause more hydrogenated C_2 products, ethylene and ethane, to be produced and also appear to eliminate the need for oxygen and reduce the need for hydrogen to present.

For each of the reaction configurations under study, a general plan was used to help focus the effort on advancing the knowledge. The general schematic (here for DC non-dielectric conversion) is shown on the next page. Of course, not all of these blocks are as independent of each other as might appear here. When sufficient adverse results were obtained, specific avenues were discontinued. The focus during the course of this project has been primarily on reactor configurations and operating variables that assisted determination of the pathways and selectivity control and on improving power use. This included some effort on catalyst development and also higher pressure operation. Essentially no work was devoted to development of process configurations that would allow preliminary economics to be determined (other than gross power requirements).

Electrical power consumed is reported in eV/methane molecule converted. 1 eV/molecule is approximately equal to 29 kWh/1000 scf converted (and 1 MMBtu is 293 kWh). For reference, the literature indicates that conventional processes to produce methanol or Fischer-Tropsch Synthesis have *net* energy consumptions of about 140 and 310 kWh/1000 scf, respectively¹. We have demonstrated values for energy consumption at or below those of conventional processes in some cases. Our best is about 90 kWh/1000 scf converted and there have been continuous improvements. This is gross energy use, with no optimization of the power system or heat recovery. While this is only one measure of the potential for an economic process, these results indicate that a traditional limitation of plasma systems can be overcome. Even in our results where energy consumption is higher, the advantages of low temperature processes, such as much lower capital costs for gas heating and cooling, and potentially higher single pass conversions may overcome this disadvantage.

With this introduction, the following sections present summaries of the major results of the primary avenues of research undertaken during this project.

¹ Rostrup Nielson, J. R., *Catalysis Today*, **21**, 257 (1994)

Section II.

Summary of DC Tubular Reactor Results (C₂ plus Syn Gas)

Objectives

Cold plasmas or "non-equilibrium" plasmas have been shown to activate methane at temperatures as low as room temperature. The catalytic dc system¹ has shown to be an effective method in the conversion of methane at room temperatures while maintaining high selectivities. The system can produce high selectivities of C₂ hydrocarbons, hydrogen, and synthesis gas. The purpose of this study was to determine how the product distribution is affected by operating in a non-oxidative environment and an oxidative environment. The non-oxidative feed produces C₂ hydrocarbons and hydrogen, while the oxidative environment yields synthesis gas and a lesser amount of C₂'s. Another valuable feature of this system is the very low concentrations of carbon dioxide and water formed, even under the oxidative conditions.

Conditions

The reactor's electrode configuration consists of a point to plane geometry, meaning that the top electrode is a wire point electrode, located axially in a vertical tube, 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 residence times range from 0.3 seconds to 2.6 seconds. The catalyst, X or Y zeolite, is loaded from the top onto the flat plate lower 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 to keep the catalyst bed uniform due to the

electrostatic nature of the zeolites and the plasma itself. The preparation and characterization of these zeolites has been discussed elsewhere^{2, 3}. The power is varied between 3 and 6 watts.

The preliminary research involved the studying of the effects of low temperature dc plasma with many different catalysts. A wide range of metal oxide catalysts and zeolites has been investigated^{4, 5}. It has been shown that the use of catalysts with the streamer discharges allows for higher activity than would occur with either catalyst or discharge independently. The catalysts containing polar OH groups result in the highest activity when coupled with the electric discharge. This led to the investigation of zeolites that have high activity when coupled with the gas discharge at low temperature. The acidic zeolites, such as ZSM-5, have high activity but coke up rapidly, while basic zeolites coke at a much slower rate while maintaining high activity. The majority of this work was done using basic zeolite catalysts, in particular NaX and NaY zeolites.

Principal Results

The initial studies involving the effect of temperature and feed composition are summarized in several articles¹⁻³. Methane conversion decreases and oxygen conversion increases with an increase in temperature. Thermal effects dominate as the temperature is increased, and carbon monoxide and carbon dioxide production increases. Early studies used helium as a diluent to reduce coke formation and allowed for high fractional conversions. It was in these studies that showed how the activity depended on oxygen concentration.

Effect of Oxygen Concentration

The effect of oxygen on methane conversion was studied using X zeolite^b. Figure 1. Once the electric gas discharge has begun, oxygen partial pressure runs below 1% begin normally but methane conversion decreases rapidly. The discharge also appears to transform into an arc discharge due to the conductivity of the carbon associated with coke formation and build-up on the catalyst. Larger concentrations of oxygen allow for the oxidation of coke to CO (only very small amounts of CO₂ are formed), resulting in a steady-state amount of coke deposited on the catalyst. While most of the experiments were done for around three hours, the stability and steady operation lasts much longer. Figure 2 shows the stability of a run performed on NaY zeolite; the X and Y zeolites (very similar structure) behave very similarly.

Figure 1. Effect of O₂ partial pressure on CH₄ conversion. Balance He. 10 SCCM, atmospheric pressure, 40°C, 10 mm electrode gap, 0.1g NaOH-treated NaX zeolite

Figure 2. Stability of Y zeolite under plasma activation. 30 psig, 10% CH₄, 10% H₂, 1.5% O₂, and balance He

Oxygen concentrations above 2.5% do not further increase the amount of methane converted or the stability; however, an increase in oxygen does reduce the selectivity towards C₂'s, as seen in Figure 3. The higher concentrations of oxygen in the feed results in an over oxidation of the carbon species towards CO, Figure 4.

Figure 3. Effect of O₂ partial pressure on C₂ selectivity. Balance He. 10 SCCM, atmospheric pressure, 40°C, 10 mm electrode gap, 0.1g NaOH-treated NaX zeolite

Figure 4. Effect of O₂ partial pressure on CO selectivity. Balance He. 10 SCCM, atmospheric pressure, 40°C, 10 mm electrode gap, 0.1g NaOH-treated NaX zeolite

Effect of Pressure

Some initial studies of the effect of pressure have also been performed. These experiments, such as shown in Figure 2, were done with helium as a diluent. Figure 5 shows how the methane reaction rate depends on the total system pressure. The methane reaction rate doubles as the pressure is doubled from 1 to 2 atm. This is due to the doubled throughput of methane at the same residence time, while the fractional conversion remained constant. Further increases in pressure did not result in an increase in reaction rate.

Figure 5. Effect of pressure on reaction rate.

Effect of the Feed Composition

As shown in the previous studies plasma discharge, or cold plasma, is very effective in the conversion of methane at low temperatures. Since helium is not a practical feedstock for processes, the helium was removed from all future experiments. 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. In addition, a feed composition of 80% methane and 20% oxygen was tested at the same conditions to compare the conversions and selectivities in a "non-oxidative" and "oxidative environment". It is presumed that the 20% oxygen in the second set of experiments and the hydrogen in the first set of experiments play an important role in a continuous cleaning of the catalyst, which plays an important role in the stability of the streamer discharges.

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.

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.

Hydrogen, acetylene, and carbon monoxide are still the major products of the 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.

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. 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.

Figure 7. Hydrogen selectivity and yield for the two different feed compositions at different residence times. Feed compositions of 2/1 H₂/CH₄ with 2% oxygen or 4/1 CH₄/O₂; gas temperature, 298 K; power, 5.2 watts.

Figure 8. Acetylene selectivity and yield for the two different feed compositions at different residence times. Feed compositions of 2/1 H₂/CH₄ with 2% oxygen or 4/1 CH₄/O₂; 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 H₂/CH₄ with 2% oxygen or 4/1 CH₄/O₂; gas temperature, 298 K; power, 5.2 watts.

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.

Effect of Streamer Bypassing

Figure 10 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 10. 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 10 show that the larger reactor has a lower conversion than 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 solid line drawn on Figure 10 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.

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 11 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 variance.

Figure 11. 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.

The acetylene selectivity, seen in Figure 12, 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 13, goes through a maximum at the intermediate residence times.

Figure 12. 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 13. 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.

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, 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.

Summary

In conclusion, the catalytic plasma conversion of methane is an effective method for the conversion of methane to valuable products such as C_2 hydrocarbons, hydrogen, and carbon monoxide. For the non-oxidative system, conversions as high as 70% at a residence time of 2.6 seconds, while maintaining acetylene, hydrogen, and carbon monoxide selectivities of 65%, 75%, and 20%, respectively. The methane conversion for the oxidative system at a residence time of 2.6 seconds is 55%. The selectivities for acetylene, hydrogen, and carbon monoxide are 55%, 75%, and 40%, respectively. Higher system pressure results in an increase in the reaction rate of methane at a given residence

time. Reaction rates doubled due to the doubling in throughput of methane while maintaining the same conversion from 1 to 2 atm. Energy use as low as 15 eV/molecule CH_4 converted have been achieved.

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Section III.

Summary of AC Tubular Reactor Results (C_2 plus Syn Gas)

Objectives

Experiments using a low temperature AC discharge within a quartz tube reactor were initiated in an attempt to directly form more valuable products from the partial oxidation of methane. Oxygen is included in the methane feed to increase the activation rate of methane. The products for this particular reaction are essentially limited to hydrogen, ethane, ethylene, acetylene, CO, CO_2 , and water. The rate of methane conversion and product selectivities can be controlled by changing various reaction parameters. The objective of the study is to maximize the conversion of methane to C_2 species and/or synthesis gas and to minimize the energy consumption.

Reactor Configuration

In this system, no dielectric barrier between the electrodes is used. In contrast to SED reactors, no physical barrier is present to control the current passing between the electrodes. The discharge occurs at a single point on the electrode each time the breakdown voltage is surpassed. Therefore, the discharge zone is confined to a relatively small volume. In order to prevent most of the feed gases from bypassing the reaction zone, the electrode area and reactor volume are greatly reduced. This is accomplished by placing two electrodes, spaced axially, in a quartz tube. The top electrode has a point configuration while the bottom electrode is a small flat disk (planar). The tip of the point electrode is free to move in the radial direction opposite the bottom electrode. The tip of the electrode can be manipulated with the use of an exterior oscillating magnetic field to move along a path in a plane parallel to that of the bottom electrode (generally side to

side). The feed gases flow axially through the discharge zone. Several reaction parameters can be varied to test their effect on methane conversion and product selectivity. The ranges for the various parameters are as follows:

Parameter	Range
Frequency	100 - 350 Hz
Point Electrode Movement	static or oscillating
Oxygen Fraction	0 - 33 %
Power	10 - 40 W
Quartz tube ID	4.5 and 7.0 mm
Pressure	0 - 15 psig
Residence Time	0.05 - 1.2 sec.

Principal Results

A base "standard" experiment 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 1.0 cm. This resulted in a residence time of 0.231 seconds. The frequency of the applied voltage was fixed at 300 Hz. The minimum power needed to maintain a stable discharge in the reactor was about 8 W. The power for this experiment was set at 10 W. The total methane conversion for this experiment was 24.4% and the oxygen conversion was 49.2%. The methane conversion efficiency was determined to be 6.8 eV per molecule of methane converted. 52.3% of the hydrogen from the reacted methane formed molecular hydrogen. The carbon based selectivities were as follows:

Component	Ethane	Ethylene	Acetylene	CO	CO ₂
Selectivity	7.4%	15.4%	16.7%	40.0%	5.2%

Almost half of the carbon from the converted methane formed carbon monoxide. Another 40% formed C₂ hydrocarbons while less than 6% became CO₂.

A series of experiments were performed to test the effect of changing the frequency of the applied voltage. All of the previous reactor parameters were held constant while the frequency was varied between 150 and 350 Hz. The voltage was adjusted during each experiment to maintain a constant power of 10 W. The total methane and oxygen conversion did not change for these experiments. The selectivities of the gas products were also the same for each frequency. Although the conversions and product ratios did not change, the experiments performed at 300 and 350 Hz were more stable; that is, the discharge was never altered by the formation of carbon along the inside of quartz tube in the reaction zone. Experiments at lower frequencies saw the formation of electrically conductive carbon filaments - these filaments conducted the current along walls of the tube thereby significantly reducing the number of high energy electrons within the reaction zone.

The AC discharge within the quartz tube looks like a small cluster of fine bluish sparks between the electrodes. These sparks, often called streamers, occupy a relatively small fraction of the total reactor volume. It is believed that a large fraction of the feed gas may bypass these streamers and may not interact with the energetic electrons needed for activation. In order to decrease the feed gas bypassing with the reactor volume, the point electrode was forced to oscillate back and forth within the reactor by means of an external magnet. The streamer discharges moved through a larger fraction of the reaction zone as the point electrode moved from one side of the quartz tube to the other. Although the conversion efficiency improved little using the oscillating electrode, the formation of excessive coke within the reactor became less problematic, resulting in a more stable discharge.

The next series of experiments was designed to test how the concentration of oxygen in the feed affects the conversion of methane and the distribution of products. The frequency was set at 300 Hz to minimize carbon formation within the reactor and the oxygen concentration was varied between 5% and 33% (set below the Lower Explosion Limit). The other reactor parameters were the same as before. Figure 1 shows that the addition of oxygen is very 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 some of the major products. Figure 2 shows that the hydrogen selectivity does not change significantly for these experiments - remaining between 50% and 60%. But the selectivities of the 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 distribution of C₂ species also changes as the feed oxygen concentration changes. 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.

Figure 1 - Conversion and Efficiency vs. Oxygen Fraction in Feed for AC tubular reactor

Figure 2 - Product Selectivities vs. Oxygen Fraction in Feed for AC tubular reactor

Other experiments were performed to test the effect of increasing the applied power on the conversion of methane. While the total methane and oxygen conversions increase with increasing power, the average energy required to convert each methane molecule increases. Excessive coking also becomes a problem at higher powers. It is thought that the reactor temperature increases significantly as the power consumption increases. At higher temperatures, the thermal reaction of methane to form coke becomes more prevalent. These carbon deposits tend to form along the inner wall of the quartz tube. Since the coke is electrically conductive, the current tends to flow through the carbon. This limits the number of energetic electrons that can interact with the feed gases in the reaction zone, thereby lowering the efficiency of the reaction.

The next experiment attempted to reduce gas bypassing within the reactor by reducing the inner diameter of the quartz tube. This would constrict the flow of the feed gases, thereby increasing the probability that the feed gases contact the energetic electrons needed for activation. The quartz tube used for this experiment had an inner diameter of 4.5 mm. The ratio of methane to oxygen in the feed was set at 2:1. All other

reaction parameters were the same as the "standard" experiment. The following is a comparison of the results from the 4.5 mm tube and the 7.0 mm tube:

Tube ID	Methane Conversion	Oxygen Conversion	eV per molecule of CH ₄ converted
4.5 mm	50.5%	81.5%	4.1
7.0 mm	42.8%	65.5%	5.5

	Selectivities					
Tube ID	H ₂	Ethane	Ethylene	Acetylene	CO	CO ₂
4.5 mm	50.0%	2.9%	10.4%	19.6%	53.3%	6.8%
7.0 mm	54.0%	3.4%	9.7%	14.0%	55.1%	6.0%

Both the methane and oxygen conversions increase using the 4.5 mm tube. The conversion efficiency improves from 5.5 to 4.1 eV per molecule of CH₄ converted. The product ratios, however, essentially remain the same.

The next experiment was designed to determine the effect of increasing the reactor pressure on methane conversion and product selectivity. A backpressure regulator was used to set the reactor pressure at 15 psig. The feed gas was a methane and oxygen mixture at a 3:1 ratio and the flow rate was raised to 200 SCCM to maintain a similar residence time as the "standard" experiment. The quartz tube ID was 7.0 mm and the electrode spacing was 1.0 cm. The minimum voltage required for electric breakdown in the reactor increases with pressure. This means that the minimum power required to obtain a stable discharge increases as well. The power for this experiment was set at 18 W. The conversion and selectivity data is summarized by the following:

Pressure	Methane Conversion	Oxygen Conversion	eV per molecule of CH ₄ converted
0 psig	24.4%	49.2%	6.8
15 psig	31.3%	75.9%	5.4

Pressure	Selectivities					
	H ₂	Ethane	Ethylene	Acetylene	CO	CO ₂
0 psig	52.3%	7.4%	15.4%	16.7%	40.0%	5.2%
15 psig	62.3%	3.0%	9.4%	21.6%	43.7%	10.0%

This data shows that the high pressure experiment operated more efficiently than the low pressure experiment in terms of methane conversion. Also, the selectivities of hydrogen, acetylene, and CO₂ increased while ethane and ethylene decreased. The CO selectivity remained about the same.

Another series of experiments has tested the effects of residence time. The reaction parameters were the same for the "standard" experiment, except the flow rate of the feed gases was varied between 50 and 400 SCCM. The conversion and efficiency data is shown in Figure 3. Although the overall conversion of methane increases as the residence time increases, the reaction becomes less efficient. Since the reaction rate of methane is a function of the methane and oxygen concentration, the overall rate of methane conversion is highest at low residence times. The methane and oxygen concentrations remain relatively high through the reaction zone. As residence times increase, the overall conversion of methane and oxygen increase. The fractions of methane and oxygen are smaller; therefore the average reaction rate decreases. This lowers the overall efficiency of the reaction. The product selectivities did not change significantly over the range tested.

Figure 3 - Methane and Oxygen Conversion and Efficiency vs. Residence Time for the AC tubular reactor

Summary

A wide range of reaction parameters have been varied to test their effects on methane conversion and product selectivity in the AC tubular reactor. The results indicate that increasing the oxygen fraction in the feed (while remaining safely below the Lower Explosion Limit) enhances the activation of methane in the reaction. Also, reducing feed gas bypassing, minimizing power, and increasing the reaction pressure all seem to improve the efficiency of methane conversion. Up to this point, the best results have come using these reactor conditions: a feed mixture of methane and oxygen at a 2:1 ratio flowing at 200 SCCM through a quartz tube with an inner diameter of 4.5 mm. The gas gap between the electrodes was 1.0 cm. This resulted in a residence time of 0.151 seconds. The reactor pressure was 0 psig (1 atm). The frequency of the applied voltage was fixed at 300 Hz and the power was set at 10 W. The overall methane conversion was 30.0% resulting in an efficiency of 3.7 eV per molecule of CH₄ converted. The product selectivities are as follows:

Component	H ₂	Ethane	Ethylene	Acetylene	CO	CO ₂
Selectivity	51.5%	4.9%	11.2%	19.4%	47.6%	4.9%

There are a number of ways to improve these "best" results. This includes raising the reaction pressure, decreasing the tube ID further, decreasing residence time, and changing the electrode gap distance. Continuing work will focus on improving the reaction efficiency with the goal of establishing a reactor design that can compete with current methane conversion technologies.

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Section IV.

Summary of AC Dielectric Partial Oxidation Results (Oxygenates plus Syn Gas)

Objectives

The direct partial oxidation of methane to methanol is a desirable potential industrial process for the future. We are using a dielectric barrier discharge (DBD) reactor to generate a non-equilibrium plasma that allows the direct partial oxidation of methane to methanol to occur at ambient temperature and atmospheric pressure, therefore potentially minimizing equilibrium limitations. Our group¹⁻⁴, as well as Hunter and Gesser⁵ and Eliasson and Kogelschatz⁶, have all done research in this area. The objective of our research to date is to better understand the role of oxygen in the process, manipulate process parameters to enhance the methanol yield and energy efficiency while minimizing the CO_x yield, and gain further insight into the pathways that are present in this system. Ultimately, we will determine if this process can be used commercially. Before discussing our results, however, a brief description on the experimental conditions will be given.

Conditions

Mass flow controllers regulate the flow of feed gases to an annular reactor. The feed gas enters the reactor from the top and flows down axially through the gap between the two concentric cylinders. The inner glass cylinder has a metal foil on its inside that acts as one electrode, while the stainless steel wall of the outer cylinder acts as the other electrode. Thus, the reactor acts as a capacitor with a glass dielectric, in which uniformly distributed "micro-discharge" streams disperse throughout the volume of the reactor. The

product stream exits the annular reactor from the bottom. The outer cylinder is surrounded by a water jacket.

The reaction products are fed to a liquid trap cooled by dry ice and acetone, which produces a trap temperature of around -55°C . The primary products collected in the trap are water, methanol, formaldehyde, methyl formate, ethanol, and formic acid. Some of these products may be condensed in the reactor depending on the reactor temperature, and then are carried out by the gas stream.

The major variables in this system are feed composition, residence time, power input, and system temperature. Pertaining to feed composition, our group has examined methane, methane-oxygen, methane-oxygen-nitrogen, methane-oxygen-carbon monoxide, methane-oxygen-carbon dioxide, methane-oxygen-hydrogen, carbon monoxide-water, and carbon dioxide-hydrogen systems. Residence times ranged from 20 sec. to 3.5 min. and power inputs can range from 26 to 178 watts. The system temperature has been varied, via the water jacket, from 28 to 75°C .

Principal Results

Role of Oxygen

One goal of this research is to better understand the role of oxygen in the system. Our work has shown that when changing from a pure methane feed to a 3:1 methane-oxygen feed, with both experiments at 16 kV and 200 Hz with a one minute residence time, the methane reaction rate is increased by a factor of three.² Thus, active species generated by O_2 activate methane in the gas gap. This results in significantly enhancing the methane reaction rate. In addition, this system is dependent on oxygen activation. Replacing oxygen with CO or CO_2 shuts off the organic liquid oxygenate production and

decreases the methane reaction rate by a factor of four. This indicates that neither CO or CO₂ are able to generate the active oxygen species that enhance the methane reaction rate, nor significantly partially oxidize methane to organic oxygenate liquid products.

In addition, maintaining the partial pressure of oxygen in the reaction zone is also important. This is shown in Figure 2.

As can be seen in the figure, as the methane conversion increases, the energy efficiency decreases. This is because at higher methane conversions the partial pressure of oxygen within the reactor is lower and, therefore, the methane reaction rate decreases. Furthermore, methane coupling starts to become significant since more regions of the reaction zone are oxygen-limited.

Thus, in order to obtain a high methane conversion without losing efficiency or organic oxygenate selectivity, it is necessary to maintain the oxygen partial pressure in the reactor. Our group did this by performing three "staged" reactors in series experiments with intermediate oxygen addition. In the first experiment, a 2:1 methane-

oxygen feed was fed to the DBD reactor. For the second experiment, the feed stream was adjusted to reflect the composition of the effluent of the first experiment with liquid products removed. Furthermore, additional oxygen was added to the feed in order to reestablish the 2:1 methane oxygen feed ratio. Thus, methane, oxygen, carbon monoxide, carbon dioxide, and hydrogen were fed to the DBD reactor in the second experiment. Since trace amounts of ethane were produced in the first experiment it was not included as a feed component in the second experiment. The third experiment represented the final reactor in the series. The feed stream of the third experiment was the gas product stream of the second experiment, and oxygen was added to the feed in order for the $\text{CH}_4:\text{O}_2$ ratio to be 2:1. In all of these experiments, the frequency and power were kept constant at 174 Hz and 118 watts, respectively. The results showed that having three "staged" reactors in series with intermediate oxygen addition allowed high methane conversions with better energy efficiency results than experiments done at high methane conversion using only a single DBD reactor. The overall methane conversion for the "staged" reactor in series experiments was 59% with an average energy efficiency of 62 eV per molecule of methane converted. When using only one reactor, 53% conversion of methane required 128 eV per molecule of methane converted. In other words, the single reactor converted 10% less methane, yet was 52% less energy efficient in doing so than the three "staged" reactors in series with intermediate oxygen addition. The "staged" experiments also produced the best results our group has obtained to date in organic liquid oxygenate yield: 35%.

Effects of Temperature

Developing a viable process has been a goal of this research. Using reactors in series with intermediate oxygen addition, as described above, helps further this objective. Another important process parameter is the temperature within the reactor. As seen in Table 1, as the temperature decreases from 75 °C to 28 °C, the organic liquid sum more than doubles.

Table 1: Cylindrical Reactor, 3:1 CH₄:O₂, 7.6 kV, 100 hz, 200 cc/min flow rate

H ₂ O Temp. ° C	Mole % CH ₄ Conv.	Mole % O ₂ Conv	% Ethan Select.	% CO Select	% CO ₂ Select	% Me Select.	% MF Select.	% FA Select.	% F Select.	% Et Select.	%Org. Liquid Sum	%Gas Phase Sum
28	24	74	4	14	13	17	5	16	13	1	52	31
54	24	81	4	25	22	9	5	12	7	1	34	51
75	25	88	3	36	26	9	4	7	4	0	24	65

Note: Me=Methanol, MF = Methyl Formate, FA = Formic Acid, F = Formaldehyde, Et =Ethanol

This increase occurs because, as the temperature in the reactor decreases, the saturation pressure of the organic oxygenates also decrease. Thus, the fraction of organic oxygenates in the liquid phase increases which, therefore, decreases the probability of over-oxidation taking place.

Effects of Recycle

By using a recycle at a high recycle ratio and low residence time per pass with removal of the organic oxygenates via a liquid trap, we can further enhance the organic oxygenate liquid production. This is because the duration these products are in the active zone decreases and, therefore, reduces their chances of becoming over-oxidized to CO or CO₂. As shown in Table 2, the recycle experiment's selectivity toward organic oxygenate products was 11% greater than in the non-recycle experiment, while the CO_x selectivity was decreased by 19 %.

Table 2. Recycle Experimental Results

Power = 118 W, Freq. = 174 Hz, Water Temp. in Jacket = 28 °C, CH ₄ :O ₂ Flow Rate Input Ratio = 2.5:1										
Recycle Ratio	% C Selectivity (mole Basis)									
	CO ₂	CO	Et	Pr	n-B	Me	MF	FA	F	El
0	13	19	13	3	1	6	8	19	11	1
160	15	11	4	0	0	17	5	12	10	7
Et = Ethane, Pr = Propane, n-B = n-Butane, Me = Methanol, MF = Methyl Formate, FA = Formic Acid, F = Formaldehyde, El = Ethanol										

In addition, the recycle experiment suggested that methane was directly oxidized to CO_x since the production of CO_x continued.

Effects of Pressure

Using pressures greater than atmospheric might increase the energy efficiency and the organic liquid oxygenate yield. This is because increasing the pressure increases the concentration of methane and oxygen in the feed. Thus, increasing the feed concentration, while holding the power input constant, might lead to an increase in the methane reaction rate and, therefore, the energy efficiency. Higher pressures also increase the driving force for condensation within the reactor. Therefore, this should enhance the organic liquid oxygenate selectivity. Preliminary results, shown in Table 3, support these theories on the effects of pressure.

Table 3. Preliminary Pressure Experimental Results

Power = 118 watts, Feed Ratio = 4:1 CH ₄ :O ₂ , Residence Time = 38 sec., Gas Gap = 1.9 mm gap, Water Temp. in Jacket = 28 °C			
Reactor Pressure (atm.)	eV per molecule of methane converted	Mole % methane converted	Organic oxygenate liquid sum
1	62	16	60
2	48	10	71

More experiments at higher pressure will need to be done in order to better define the effects of pressure.

Effects of Nitrogen

Methane/oxygen-enriched-air systems have also been studied. Increasing the $N_2:O_2$ ratio in the feed causes the energy efficiency to decrease because the methane throughput is decreasing. Economic calculations still need to be made to determine if the benefits of omitting pure oxygen in the feed outweigh the loss in energy efficiency and desirable product selectivity.

In addition, increasing the nitrogen partial pressure in the feed increases the CO_x production. The organic oxygenate liquid sum, however, does not decrease, as would be expected if over-oxidation of these products were occurring. Therefore, currently we do not have a good explanation of why this is happening.

Water-Gas Shift & Reverse Water-Gas Shift Reactions

It has also been shown in previous work that the water-gas shift and reverse water-gas shift reactions are present^{2,3}:

Feeding a 3:1 methane-oxygen stream with carbon dioxide to the DBD reactor results in shifting the CO_2 selectivity to CO. This is due to the reverse water-gas shift reaction as well as CO_2 being directly converted to CO and O_2 . When 20 mole % or more of CO_2 is in the feed, the net production of CO_2 is less than the net destruction of CO_2 . When 30 mole % of CO_2 is present in the feed, there is a significant decrease in the organic liquid production as a result of the system becoming oxygen-limited.

Methane-oxygen-carbon monoxide systems show the same trends as methane-oxygen-carbon dioxide systems except that the selectivity shifts from CO to CO_2 when

the concentration of CO is increased in the feed. This occurs because of the water-gas shift reaction and CO being oxidized to CO₂ by O₂.

When the feed partial pressure of hydrogen is increased in a methane-oxygen-hydrogen system, the hydrogen conversion and carbon dioxide selectivity increases. This indicates that the hydrogen reacts with the oxygen and forms water. The water-gas shift reaction is only a secondary reaction that takes place.

Summary

In conclusion, we now have more insight into the pathways that are occurring within the system. We have shown that oxygen rather than carbon monoxide or carbon dioxide is needed to oxidize methane to organic liquid oxygenates. This is because the organic liquid oxygenate production is negligible when oxygen in the feed is replaced with carbon monoxide or carbon dioxide. In addition, the water-gas shift and reverse-water gas shift reactions are chemical pathways that exist in the system. Thus, increasing the partial pressure of CO₂ in the feed causes a shift in selectivity to CO via the reverse water-gas shift reaction and the direct conversion of CO₂ to CO and O₂.

We have also studied some factors that need to be considered when designing a process. Compared to a single reactor, high methane conversions to organic liquid oxygenates with increased energy efficiency can be obtained by using reactors in series with intermediate oxygen additions. In addition, operating at ambient temperature within the reaction zone increases the fraction of organic oxygenates within the reactor, therefore, enhancing their yield by reducing over-oxidation. Further enhancement in the liquid production can occur by using a recycle at a high recycle ratio with organic oxygenate removal via a liquid trap. This is because the duration the organic oxygenates

remain in the gas phase is minimized. Finally, using a methane/oxygen-enriched-air feed might improve the economics of the system, but an in-depth economic analysis still has to be done in order to determine the true economics of the system.

The best result our group has obtained in the silent electric discharge reactor is 46 eV per molecule of methane converted with some selectivity toward CO₂. We have also obtained methane conversions, organic liquid selectivities, and organic liquid yields as high as 59%, 71%, and 35%, respectively. The current industrial process, steam reforming of methane to synthesis gas and then methanol, requires only 11 eV per molecule of methanol produced.⁷ However, a modest improvement in energy consumption and the other advantages of the operating conditions of this system could result in an economically feasible process.

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Section V.

Summary of AC Dielectric Hydrocarbon Results (Higher Hydrocarbons)

Objectives

The thermal reaction of methane to form higher hydrocarbons occurs only at high temperatures (> 1000 K) and/or extreme pressures¹. At extreme temperatures, the formation of C_2 olefins and carbon is favored over the formation of C_3+ paraffins. The dielectric barrier discharge, commonly referred to as a *silent electric discharge (SED)*, has been shown to activate methane at ambient temperature and pressure. The activated methane may then react to form higher hydrocarbons and hydrogen. Unlike the thermal reaction of methane, the formation of paraffins is favored over the formation of olefins. The primary purpose of this study is to determine the feasibility of a process for the conversion of methane to higher hydrocarbons and hydrogen using a silent electric discharge. This includes maximizing the conversion of methane using the SED reactor, studying the distribution of products, and minimizing the energy consumption for the reaction. Another important objective of this study is to gain a greater understanding of the effect of reactor and power variables as well as chemical pathways. This understanding is developed by determining the density and average energy of the high energy electrons generated within the reactor, investigating how these high energy electrons activate the feed gases, and learning how the activation rates can be changed by manipulating the various reaction parameters.

Reactor Configuration

The silent electric discharge occurs in the gas gap between a pair of electrodes that have similar geometry, that is, between two flat-plate electrodes or in the annulus

between two concentric cylindrical electrodes. A dielectric barrier that is often made of glass must cover at least one of the electrode surfaces. The reactor geometry (gas gap distance, dielectric thickness, electrode structure) can be changed so that the various geometric effects can be tested. The flat plate SED reactor system consists of two metal electrodes made from flat metal plates. A dielectric barrier made of glass covers one electrode surface. A Teflon or nylon spacer is situated around the periphery of the reactor between the dielectric and the opposite electrode. This spacer provides a gas gap between the exposed electrode and the dielectric for the inlet gases to flow axially through the reaction zone. The electrical and geometric parameters can be varied to test their effect on methane conversion and product selectivity. The ranges for the various parameters are as follows:

Parameter	Range
Frequency	50 - 300 Hz
Power	0 - 150 W
Waveforms	Sine, square, and triangular
Dielectric Thickness	2.29 - 5.82 mm
Residence Time	0.5 - 15 min.
Gas Gap Thickness	0.84 - 12.7 mm
Pressure	0 - 10 psig

Principal Results

Initial experiments with the SED reactor were conducted using a feed of pure methane. The dielectric barrier was a glass plate with a thickness of 2.97 mm and the spacer was made of teflon and had a thickness of 1.78 mm. The residence time for this experiment was about 6.5 minutes. The frequency of the alternating current for these initial experiments was 60 Hz. Figure 1 shows that the methane conversion increases

significantly as the applied voltage increases. However, the selectivities of the products essentially remain the same.

Figure 1 - Typical Methane Conversion and Product

The initial experiments with the dielectric barrier reactor confirm that the silent electric discharge is capable of converting a significant amount of the pure methane feed to higher paraffins at ambient temperature and pressure. This type of reaction can produce concentrations of higher paraffins and hydrogen at similar ratios to the thermal reaction of methane occurring at over 1700 K. Also, the silent electric discharge appears to suppress the dehydrogenation reactions that form C_2 olefins that dominate the thermal reaction of methane at temperatures above 1000 K. Under these reaction conditions the power required to convert the methane is high, the best being about 300 eV/molecule CH_4 converted, and the residence times are long, on the order of minutes, to be optimistic that an industrially feasible process is likely.

Figure 2 – Equilibrium Product Distribution for Reaction of Pure Methane (to paraffins and olefins)

Figure 3 – Equilibrium Product Distribution for Reaction of Pure Methane (paraffins only)

No methane conversion occurs at voltage potentials below the breakdown voltage. The breakdown voltage for this particular set of experimental conditions is approximately 4,000 volts. Below the breakdown voltage, no current passes through the reaction zone. No high energy electrons are available to activate the methane molecules, therefore, methane conversion does not occur. At potentials above the breakdown voltage, high energy electrons collide with methane molecules in the gas gap and are capable of creating activated methyl species that can then react with other methane molecules to form carbon-carbon bonds. A hydrogen molecule is also produced when a carbon-carbon bond forms.

These pure methane experiments suggest that the predominant reaction pathway for this feed condition begins when an activated C_1 species reacts with another C_1 species to ultimately form ethane and hydrogen. An activated C_2 species can react with a C_1 species to form propane or react with another C_2 species to form butane. Since olefin production is very low, it is apparent that dehydrogenation reactions are not favored

under these conditions. Also, the reaction of dehydrogenated C_1 species (such as CH_2^*) to form unsaturated products is not significant. At higher methane conversions, the partial pressures of C_2+ species become large enough to have a recognizable effect on the reaction. The chain scission rate of the C_2+ species to reform methane becomes large enough to begin limiting the overall methane conversion.

Effect of Power

Other experiments using the flat plate reactor were initiated to determine the effect of varying the frequency of the applied voltage on methane conversion and product selectivity. The dielectric barrier in the reactor was nearly twice as thick as that used in the preliminary experiments. The glass plate used in this set of experiments had a thickness of 5.82 mm. The spacer thickness was the same at 1.78 mm thick. The applied voltage was held constant while the frequency of the sinusoidal waveform was raised from 50 Hz to over 300 Hz. Figure 4 shows that no reaction occurred in the reactor until the frequency was raised to over 130 Hz. Both the methane conversion and the power consumption by the reactor increased with increasing frequency until about 180 Hz. As the frequency was raised further, the methane conversion and power usage decreased until the reaction stopped at frequencies over 300 Hz.

Figure 5 indicates that methane conversion within this type of reactor system may be expressed as a function of the power consumed by the reactor. The methane conversion varies linearly with the power consumed by the reactor system. At low frequencies (<125 Hz), the power consumption is very low because the power factor is very small. The power factor is simply the cosine of the phase difference that exists between the applied voltage and the current. The power factor varies with frequency due

to the capacitive nature of the reactor. At frequencies above 125 Hz, the magnitude of the power factor begins to increase. The power consumed by the reactor increases as does the methane conversion within the reactor. The methane conversion increases linearly with power until maximum power consumption is achieved at about 180 Hz. At this point, the power factor and the power consumption decrease as the frequency of the applied voltage increases. Again, the methane conversion varies linearly with changes in the power. At frequencies above 300 Hz, the power factor becomes very small. The power in turn is very low and breakdown within the reactor ceases, terminating any methane conversion. It should be noted that the methane conversion varies linearly with power only for relatively low methane conversions (<~30% conversion). As the total methane conversion gets larger, the methane conversion becomes less dependent on changes to the power. Chain scission reactions of the higher hydrocarbons limit the total methane conversion, causing the methane conversion vs. power curve to flatten out.

Figure 4 - Methane Conversion and Power vs. Frequency for an SED reactor

Figure 5 - Methane Conversion vs. Power Consumption for an SED reactor

The next series of experiments focused on determining what effect the type of waveform (sine, square, and triangular) might have on power consumption by the reactor, methane conversion within the reactor, and the selectivities of the various products. Figure 6 illustrates that there is no significant difference between the curves generated by the sine wave and the triangular wave. The power factors measured for the sine wave and the triangular wave vary little over the entire range of frequencies tested. The maximum magnitude of the power factor for these two types of waves, measured between 180 and 190 Hz, is about 0.99. This resulted in maximum power measurements around 75 watts. The maximum power factor for the square wave, however, is less than that for the sine and triangular waveforms. It's maximum is 0.91 which occurs between 190 and 200 Hz. The maximum power consumption for this case is about 61 watts. Another local maximum along the power vs. frequency curve for the triangular and square waveforms occurs at about 90 Hz. These slight increases in the power consumption for this small range of frequencies are due to small localized increases in the respective power factors for these two waveforms.

Although the maximum power consumption for each of these waveforms differs to some extent, the linear relationship that exists between methane conversion and the power used by the reactor does not change for any of these waveforms. The methane conversion is the same for the same power values, no matter which waveform is used. The product selectivities are also not measurably different for any waveform. Although the sine wave may appear to be more "efficient" than the other waves because it can reach the highest power factor and power consumption measurements for a given applied voltage, the efficiency of the methane conversion is no better.

Figure 6 - Power Consumption vs. Frequency for three different wave forms

Effect of Geometry

Experiments on the effect of reactor geometry on methane conversion were initiated by varying the thickness of the glass plate used as the dielectric barrier within the reactor. Many of the previous experiments were conducted using a glass plate with a thickness of 5.82 mm. As stated earlier, the magnitude of the power factor was not great enough to provide sufficient power to the reactor to initiate breakdown until the frequency was raised to over 130 Hz. However, breakdown occurred at the same applied voltage in some of the preliminary experiments at 50 Hz using a thinner dielectric. This suggested that there might be an optimum dielectric thickness for the dielectric barrier reactor.

A series of experiments that involved varying the glass dielectric thickness were performed to determine its effect on methane conversion. The power vs. frequency plots for each dielectric are seen in Figure 7. They have essentially the same shape, but the maximum methane conversion occurs at different frequencies. Each configuration has its own "optimum" frequency where maximum methane conversion takes place.

However, the maximum methane conversion obtainable for a given applied voltage is the same for each configuration. The slope of the methane conversion versus power curve also did not change. This means that changing the thickness of the dielectric does not improve the efficiency of the reaction. The product selectivities are the same for each configuration as well. This suggests that the dielectric thickness does not change the number or energy level of the electrons in the microdischarges that are able to activate methane for a given power input. The sole purpose of the dielectric is to control the charge transfer across the gas gap between the electrodes. As long as the dielectric barrier is sufficiently large to prevent breakdown within the dielectric itself, the silent electric discharge will operate properly. However, different reactor geometries can be "tuned" to an optimum frequency to obtain maximum power usage and methane conversion for an applied voltage.

Figure 7 - Methane Conversion vs. Frequency for SED reactors with different dielectric thicknesses

The next series of experiments tested how changing the exposed electrode surface in the reactor might alter the nature of the reaction. Initial experiments used a metal electrode with a smooth surface. Later, this electrode was replaced with an electrode that had five grooves along its entire length. These grooves were initially intended to collect and channel any liquid products that may have formed within the reactor away from the reaction zone. Since the partial pressure for any condensable products is so low for these hydrocarbon reactions, these channels are not needed for this purpose. It should be noted, however, that charge tends to collect along the edges of the electrodes. It was suspected that this may have an effect on the distribution of microdischarges within the reactor. Although the number of microdischarges is significantly higher along the edges of the grooves, the dielectric barrier prevented the microdischarges from initiating solely along the edges of the grooves of the electrode. It was determined that the methane conversion and product selectivities did not differ significantly during reactions with the two different electrodes.

Experiments were conducted to test how changing the thickness of the gas gap effects methane conversion. Three different spacers were used for this series of experiments. The first was a Teflon spacer with a thickness of 0.84 mm, the second was a Teflon spacer with a thickness of 1.78 mm, and the third was a nylon spacer with a thickness of 6.35 mm. All other reactor and applied voltage parameters were held constant. Figure 8 is a plot of methane conversion vs. applied voltage for each reactor. It shows how the breakdown voltage increases as the gas gap thickness increases. As the gas gap distance increases, the dielectric strength due to the gas increases. A larger potential is needed to overcome this larger electrical barrier and break down the gas in

the reaction volume. Figure 9 is a plot of average conversion efficiency (eV / methane molecule reacted) vs. residence time for each reactor. The plot shows that the reactor with the thicker gas gap has a greater conversion efficiency than the reactors with thinner gas gaps. For a given residence time, the reactor with the thicker gas gap requires less energy to convert each methane molecule. This shows that optimizing the spacer thickness for a given reactor system plays a significant role in reducing the energy required for methane conversion.

Figure 8 - Methane Conversion vs. Applied Voltage for SED reactors with three different gas gaps

Figure 9 - Efficiency vs. Residence Time for SED reactors with three different gaps.

Although conversion is lower at the same residence time in the reactor with the thicker gas gap, the throughput is substantially increased. The selectivities for the individual products for each gas gap were not markedly different. The reaction pathways for the conversion of methane to higher hydrocarbons do not seem to change substantially with changes to gas gap thickness for a given power.

Another series of tests were designed to investigate the effect of elevated pressure on the conversion of methane in the SED reactor. The reaction pressures were set at 0, 5,

and 10 psig in the 6.35 mm gas gap reactor. The flow rates were adjusted to maintain the same residence times for each experiment. The Paschen voltage, the lowest voltage needed to initiate breakdown within the reactor, increases as the pressure increases. Therefore, a larger applied voltage was necessary to maintain the same power consumption for the reactions at higher pressures. The results show that the net methane conversion rate is essentially the same for each pressure tested. The conversion efficiency was 264 eV/mol. at 0 psig and 272 eV/mol. at 10 psig, varying less than 4%. Since the primary products were paraffins and hydrogen, the product selectivities did not vary substantially with pressure.

Hydrocarbon Reactions

Since the methane molecule has proven to be so difficult to react, other paraffins ($C_2 - C_4$) were included with methane in the feed mixture to act as "initiators" for methane conversion. Figure 10 shows the net average rate of conversion for methane for some of the feed conditions tested. The percentage of methane converted is also listed for each experiment. The C_2+ paraffins reacted to form even higher hydrocarbons (C_6+) and a variety of olefins. However, the reverse chain scission reactions (cracking) to reform methane were also significant. The net rate of methane conversion was not enhanced. The addition of hydrogen to the methane feed appears to suppress the net conversion of methane. High hydrogen partial pressures increase the chain scission rates of the products to reform methane.

Figure 10 - Net Average Methane Conversion Rate for Different Feed Conditions

Summary

The silent electric discharge reactor is capable of converting over 50% of the methane feed to higher hydrocarbons. However, the energy consumption is presently too high and the residence times are too long to develop an industrially feasible process based on the current reactor design parameters. The most efficient pure methane reactions in the SED reactor have been in the 6.35 mm gas gap reactor using relatively low residence times (< one minute). The best conversion efficiencies for this system have been about 150 eV/molecule CH_4 reacted, but the per pass conversions for these experiments were less than 5%.

Since methane is a relatively stable molecule compared to the other species within the reaction environment, the rate-limiting step for the chain building process appears to be the activation of the methane molecule. The activation of methane must become more efficient before a process based upon the SED can be cost effective.

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APPENDIX

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