# Production of Organic Oxygenates in the Partial Oxidation of Methane in a Silent Electric Discharge Reactor

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This study on the partial oxidation of methane in a silent electric discharge uses an annular reactor consisting of two metal electrodes separated by a gas gap and a glass dielectric covering the outer surface of the inner electrode. The reactor operates at 7000 V and 26−178 W of AC power. The frequency ranges from 100 to 200 Hz. The organic liquid oxygenates formed from the partial oxidation of methane are principally methanol, formaldehyde, methyl formate, and formic acid. This study showed that, when the oxygen partial pressure became limited in the reaction zone, the energy efficiency of the system significantly decreased. It was also shown that, with a recycle, as opposed to without, the selectivity for organic liquids was enhanced by 12%, whereas the $CO_x$ selectivity decreased by 19% because the recycle had a short per-pass residence time with removal of organic liquid oxygenate products via a condenser. Finally, experimental simulations of reactors in series with intermediate oxygen additions obtained an overall methane conversion of 59%, with 35% yield in organic liquid oxygenates.

## Introduction

Natural gas is regarded today as a very desirable fuel and chemical feedstock alternative. It is a clean resource that gives more energy per $CO_2$ molecule created than oil. It, therefore, can potentially help reduce the problem of global warming. There are vast reserves of natural gas around the world.[1] Significant amounts of these reserves are located in remote areas. Steam reforming to synthesis gas with further conversion to methanol is one major process that utilizes natural gas for its chemical value. This process, however, is very energy-intensive and might not be economical when the natural gas reserves are in remote places or when the gas is expensive.

One possible alternative is the direct partial oxidation of methane into methanol. A one-step oxidative process to methanol could substantially reduce process operating costs; however, there is presently no such process that is economically competitive.

Plasma reactors might be able to solve this problem. Studies are being conducted to determine whether these reactors can be used to control $NO_x$, $SO_x$, toxic gases, volatile organic compounds, and hazardous emissions and to synthesize ozone. For example, researchers have used plasma reactors to convert $NO_x$ and $SO_x$ to their corresponding acids. These reactors convert chemicals using either equilibrium or nonequilibrium plasmas. Plasmas are considered to be in equilibrium when the electrons and neutral species have the same kinetic energy. When the electron kinetic energies are much higher than the neutral species energies, the plasma is considered to be a nonequilibrium plasma.[2−5] Currently, research using nonequilibrium plasmas is being done to convert methane into useful products such as higher hydrocarbons, synthesis gas, and organic oxygenate liquid products.[6−12]

This study, which is a continuation of the work of Bhatnagar et al.[8,9] uses a silent dielectric barrier discharge (DBD) reactor, which creates a nonequilibrium plasma to cause the direct partial oxidation of methane. The reactor is typically operated at atmospheric pressure with an operating temperature of either 28 or 75 °C. The reactor geometry is annular with a fixed gap distance.

The ability to efficiently convert a significant amount of natural gas to useful products at a remote site is important for a process to have commercial potential. Thus, this study examines the effect methane and oxygen conversion has on the energy efficiency of the system.

In previous work, it was demonstrated that the water-gas shift and reverse water-gas shift reactions were taking place when CO or $CO_2$ was added to a methane−oxygen feed.[10,11] This work studies the influence that hydrogen has on CO and $CO_2$ selectivities via these pathways.

Earlier work has also shown that decreasing the reactor temperature increased the organic oxygenate selectivity through in situ removal of these products from the reaction zone via condensation.[11] The current work studies how the organic oxygenate selectivity is affected when a recycle stream is added. The recycle stream in this study has a high recycle ratio and low residence time per pass in which the organic oxygenates are condensed out in a low-temperature liquid trap. In addition, evidence of a direct oxidative route from methane to $CO_x$ is explored.

This study also investigates methane−oxygen−nitrogen systems to determine the effect of nitrogen on energy efficiency and product selectivity. If methanol could be produced from a methane−air feed, or from oxygen-enriched air, the cost for oxygen could be reduced or eliminated.

Finally, some types of natural gas have significant amounts of ethane within them. When ethane and oxygen are present in a DBD reactor, ethanol is one of the products formed. Currently, ethanol is regarded as a potential future fuel source. Commercially, it is

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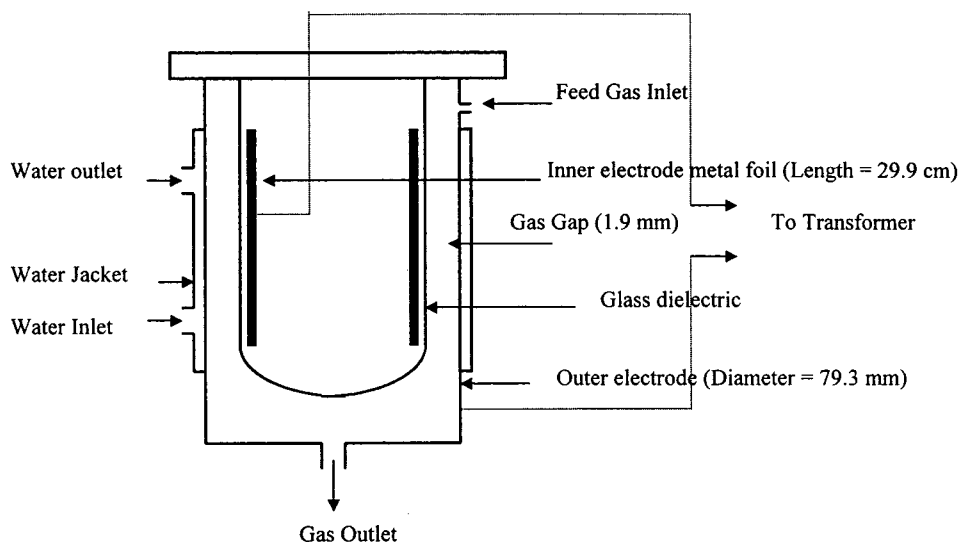* Author to whom correspondence should be addressed.

**Figure 1.** Annular reactor (effective volume = 141 cm$^3$).

produced by acid-catalyzed hydration of ethylene or fermentation.[13] This study investigates the effect of ethane composition on energy efficiency and product selectivity.

## Experimental Section

Mass flow controllers (Porter Instrument Company) regulate the flow of feed gases to an annular reactor, which is depicted in Figure 1. The feed gas enters the reactor from the top and flows down axially in the gap between the two concentric cylinders. Inside the inner glass cylinder is a metal foil 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 gap through which the gas flows is 1.9 mm. The active reaction area is 728 cm$^2$, and the effective annular volume of the reactor is 141 cm$^3$. The product stream exits the annular reactor from the bottom. The outer reactor shell is surrounded by a water cooling jacket.

The reaction products are fed to a liquid trap cooled by dry ice and acetone, which maintains the trap temperature at around −55 °C. The primary products collected in the trap are water, methanol, formaldehyde, methyl formate, ethanol, and formic acid. Some of these products might be condensed in the reactor depending on the reactor temperature and then carried out by the gas stream. Past the liquid trap, the effluent gas stream flows to an EG&G Carle Series 400 AGC gas chromatograph with a hydrogen analysis system. The exact GC protocols used for measuring products are given in Bhatnagar's work.[9] In the recycle experiments, once the gas passes through the liquid trap, most of the remaining gas is fed back to the reactor, but a small fraction exits through a purge stream that flows to the EG&G Carle Series 400 AGC gas chromatograph. The flow rates of the feed gas stream and the product gas stream are determined by using a soap bubble meter after the streams have left the condenser. The organic oxygenate liquid products are collected after the experiment and analyzed with a Varian 3300 GC on a Porapak Q column with TCD. Water is identified by the Varian 3300 GC but not quantified.

Power is supplied to the reactor with an Elgar model 501 SL AC power supply. It has a maximum power output of 500 W, and a voltage range of 0−130 V, and a current range of 0−5.8 A. The frequency range for the power supply is from 45 to 5000 Hz. The Elgar power supply is used in conjunction with a CBK precision function generator that allows for a sinusoidal waveform at the desired frequency to be generated. The voltage is stepped up 125 times through the use of a 15060 P Franceformer transformer and is applied to the reactor. Power is measured on the primary side using a Microvip 1.2 energy analyzer.

The power factor for each experiment in this work is 1, which is obtained by adjusting the frequency until this value is reached. The power input for these experiments is 118 W, except when power is the experimental variable. This power input value of 118 W was chosen in order for a significant amount of methane and/or ethane to be converted in all of the experiments that did not have power as the experimental variable. The water jacket temperature for all but one of the experimental series is 28 °C. This temperature enables in situ removal of organic oxygenates to occur within the reaction zone of single-pass systems. The experimental series that does not have a water jacket temperature of 28 °C is the hydrogen experimental series, in which the temperature is 75 °C. This higher setting is used in order to allow water that is formed in the reaction zone to remain in the gas phase and, hence, to be a potential reactant in the water-gas shift reaction.

To demonstrate that the experiments in this work can be acceptably reproduced, Table 1 compares two methane−oxygen experiments at identical conditions. The material balances (reactive molar carbon basis) for all of the nonethane experiments are fairly close to closing. However, because most of them account for 83−96% of the carbon reacted, the possibility of undetected gasphase products does exist. This is because no significant solid residue has been found within the reactor after an experiment has been completed.

In the methane−ethane−oxygen and ethane−oxygen systems, the Varian 3300 GC detects significant identified organic liquid products due to ethane chemistry. Thus, their carbon material balances are not as close

**Table 1. Experimental Reproducibility[a]**

| expt | moles of $CH_4$ conv. (mol/min) | eV per molecule of $CH_4$ conv. | $H_2$ sel. | mol % $CH_4$ conv. | mol % $O_2$ conv. | % C selectivity (mole basis)[b] | | | | | | |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | | | | | | $CO_2$ | CO | ethane | M | MF | FA | F | sum |
| 1 | .0014 | 51 | 11 | 12 | 26 | 13 | 19 | 2 | 16 | 9 | 17 | 12 | 88 |
| 2 | .0014 | 53 | 12 | 12 | 27 | 14 | 20 | 2 | 14 | 8 | 16 | 14 | 88 |

[a] $CH_4/O_2$ feed ratio = 2:1, power = 118 W, frequency = 174 Hz, residence time = 20 s, water temperature in water jacket = 28 °C. [b] M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, sum = sum of carbon selectivity.
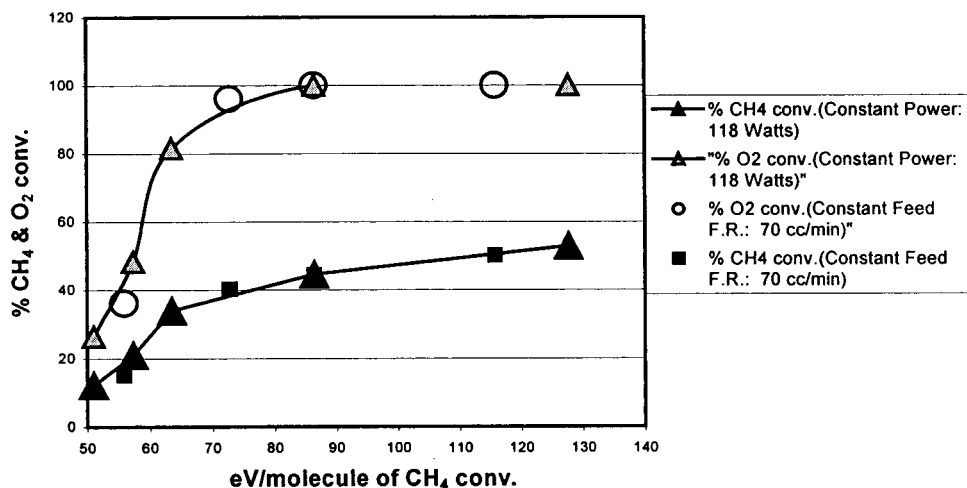


**Figure 2.** Percent $CH_4$ and $O_2$ conversion vs energy efficiency.

to closing as the rest of those of the experiments done in this work.

## Results and Discussion

**Energy Efficiency Experiments.** The first two series of experiments examine the effects of feed flow rate and power input on energy efficiency (electronvolts per molecule of methane converted) for a methane−oxygen system. For all of these experiments, the $CH_4/O_2$ feed ratio is 2:1, the water temperature in the water jacket is 28 °C, the frequency is 174 Hz, and the system pressure is 1 atm. In the first series of experiments, the power is constant at 118 W and the feed flow rate is varied from 40 to 430 cm³/min. In the second series of experiments, the feed flow rate is constant at 70 cm³/min while the power is varied from 26 to 178 W.

The results of the energy efficiency experiments are shown in Figure 2. As the methane conversion increased, the number of electronvolts per molecule of methane converted increased. The oxygen conversion, like the methane conversion, also increased, and therefore, the partial pressure of oxygen down the length of the reactor decreased. Figure 2 shows that methane conversions of 44% or greater had corresponding oxygen conversions of 100%. At these higher methane conversions, methanol production is completely shut off in the latter stages of the reactor, and methane coupling to form ethane is the predominant reaction occurring. Our previous work has shown that, when the feed is changed from pure methane to 3:1 methane/oxygen, with both experiments performed at 16 kV and 200 Hz with a 1-min residence time, the methane conversion rate (MCR), as defined below, increased by a factor of 3.[10]

$$MCR = CH_4 \text{ molar flow rate entering reactor} -$$
$$CH_4 \text{ molar flow rate exiting reactor}$$

This indicates that active species generated by $O_2$

significantly enhance the methane reaction rate, resulting in an increase in the methane conversion rate. In addition, Bhatnagar showed that increasing the partial pressure of oxygen in a methane−oxygen feed for a silent DBD reactor while keeping the residence time and voltage input constant, also resulted in an increase in the methane conversion rate.[8,9] This means that the methane reaction rate increased. Thus, lower partial pressures of oxygen in the reaction zone, through increases in oxygen conversion, lead to decreases in energy efficiency for methane conversion, as shown in Figure 2.

Figure 2 also shows that varying the power while holding the flow rate constant or vice versa produces the same energy efficiency. Thus, when the feed composition, gap distance, and system pressure are held constant, the partial pressure of oxygen is the key variable affecting the energy efficiency of the system.

Eliasson and Kogelshatz's group, in contrast, has shown that better energy efficiency at higher conversions is obtained by higher power inputs at constant flow rates, as opposed to lower flow rates at constant power inputs.[6] These results, however, were obtained at a significantly higher power input range, 100−800 W, which might suggest that, at some point, power input per surface area might significantly affect energy efficiency.

Finally, the active oxygen species responsible for the increased energy efficiency for methane conversion could be atomic oxygen, as it has been shown that a significant amount of the energy input into a DBD ozone reactor is directed toward the oxygen dissociation reaction shown below.[14]

$$O_2 \rightarrow O + O$$
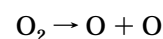
The atomic oxygen could then activate methane and form $CO_x$ or organic oxygenate liquids.

**Table 2. Hydrogen Experimental Results**[a]

| feed mole fraction | | | moles of $CH_4$ conv. (mol/min) | eV per molecule of $CH_4$ conv. | $H_{2(product)}/$ $H_{2(feed)}$ | mol % $CH_4$ conv. | mol % $O_2$ conv. | % C selectivity (mole basis)[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | $O_2$ | $H_2$ | | | | | | $CO_2$ | CO | ethane | M | MF | FA | F | sum |
| 0.67 | 0.33 | 0.00 | 0.0008 | 88 | | 29 | 81 | 38 | 42 | 2 | 9 | 2 | 0 | 0 | 93 |
| 0.53 | 0.27 | 0.20 | 0.0007 | 111 | 0.98 | 28 | 91 | 43 | 41 | 2 | 9 | 1 | 0 | 0 | 96 |
| 0.40 | 0.20 | 0.40 | 0.0005 | 156 | 0.87 | 27 | 100 | 47 | 40 | 3 | 6 | 0 | 0 | 0 | 96 |

[a] Power = 118 W, frequency = 174 Hz, residence time = 1.1 min, water temperature in water jacket = 75 °C. [b] M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, sum = sum of carbon selectivity.

## Hydrogen Experiments

Previous work[11,12] has shown that the water-gas shift reaction and reverse water-gas shift reaction, shown below, occur during the partial oxidation of methane in a silent electric discharge reactor.

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$
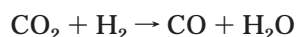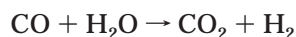
This series of experiments examines the role that these reactions play when methane, oxygen, and hydrogen are fed to the silent electric discharge reactor. The power and frequency in these experiments are set at 118 W and 174 Hz, respectively. The methane/oxygen feed ratio is kept constant at 2:1, and the total feed flow rate is 125 cm³/min. The temperature in the water jacket is 75 °C, and the system pressure is 1 atm. The hydrogen concentration in the feed is varied from 0 to 40 mol %.

Table 2 shows the results of increasing the partial pressure of hydrogen in a methane−oxygen−hydrogen feed stream in which the methane/oxygen ratio is 2:1. The results show that, when the $H_2$ concentration in the feed stream is changed from 0 to 40 mol %, the selectivity of CO remained relatively constant, whereas the selectivity of $CO_2$ increased from 38 to 47%. In both of the experiments in which hydrogen was in the feed, the net rate of hydrogen creation was less than the net rate of hydrogen destruction. This suggests that hydrogen primarily reacts with oxygen and forms water and that the water-gas shift reaction is secondary. Because hydrogen is a reactant, it cannot be regarded as a diluent. A possible reason that the CO selectivity does not significantly change is that less $O_2$ in the feed might favor partial oxidation of the organic oxygenates to CO instead of complete overoxidation to $CO_2$. Thus, CO destruction from the water-gas shift reaction is approximately balanced by CO production from the partial oxidation of organic oxygenates, as shown below.

$$CO + H_2O \rightarrow CO_2 + H_2$$
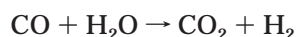
organic oxygenates $\rightarrow$ CO + noncarbon species

The number of electronvolts per molecule of methane converted increased by 44% when the hydrogen in the feed is changed from 0 to 40 mol %. This happens for two reasons. As the hydrogen partial pressure is increased in the feed, the oxygen partial pressure is decreased, which means that the average partial pressure of oxygen down the length of the reactor is lower, and the resulting lower methane activation rate lowers the energy efficiency for methane conversion. Second, as the partial pressure of hydrogen is increased in the reaction zone, the probability of oxygen reacting with hydrogen, as opposed to methane, increases. Increasing the partial pressure of hydrogen to 40 mol % also

reduced the production of organic oxygenates, as shown by the 70% decrease in the organic oxygenate products that were produced. Finally, the increase in hydrogen in the feed caused only a slight decrease in the fractional methane conversion, but because of the decreased partial pressure of methane, the methane reaction rate decreased.

**"Staged" Reactors-in-Series Experiments.** The next type of experiment is referred to as a staged experiment. The purpose is to emulate reactors in series with oxygen addition to each reactor to bring the methane/oxygen ratio back to a set value so that oxygen-depleted conditions do not occur. This is accomplished by performing single-reactor experiments in which the feed is adjusted to reflect the composition of the effluent of a reactor that would precede it, with liquid products removed and oxygen added to achieve the desired methane/oxygen ratio. Note that, because carbon oxides and hydrogen are produced, they remain in the feed to the next "downstream" reactor. The composition of the feed to a downstream reactor experiment, thus, consists of methane, oxygen, carbon monoxide, carbon dioxide, and hydrogen. The very small amount of ethane produced under these conditions is neglected. The first experiment, which represents the first reactor in series, has a $CH_4/O_2$ feed ratio of 2:1 and a feed flow rate of 225 cm³/min. The second reactor in series is experimentally emulated by making the feed stream of the second experiment the same as the gas product stream of the first experiment and adding oxygen to it so that the $CH_4/O_2$ ratio is 2:1. The third experiment represents the final reactor in the series. The feed stream of the third experiment is adjusted to the composition of the gas product stream of the second experiment, and oxygen is added to the feed in order for the $CH_4/O_2$ ratio to be 2:1. In all of these experiments, the frequency and power are kept constant at 174 Hz and 118 W, respectively.

Tables 3 and 4 show the conditions and results of the staged reactors-in- series experiments. The results show that, from stage one to stage three, the individual methane conversion for a given stage increased from 21 to 30%, making the overall methane conversion 59%. The *molar rate* of methane conversion, however, decreased by 19%. That indicates that the increase in overall methane conversion does not compensate for the decrease in methane throughput (partial pressure) in stages two and three. Thus, the energy efficiency decreased by 19% from stage one to three.

This decrease in energy efficiency occurs for two reasons. The first reason is that the methane in the reaction zone of a given stage is being converted to other carbon products, and therefore, the methane throughput to the next stage is smaller. This means that the oxygen feed partial pressure is lower than if it were fresh feed, meaning fewer active oxygen species being generated to enhance the methane reaction rate.

**Table 3. Staged Reactors in Series Experimental Results[a]**

| stage | feed mole fraction | | | | | res. time (s) | $CH_4/O_2$ | eV per molecule of $CH_4$ conv. | moles of $CH_4$ conv. (mol/min) | mol % $CH_4$ conv. | mol % $O_2$ conv. | $H_2/CO$ | $H2/CO_2$ | $H_2$ sel. |
| | $CH_4$ | $O_2$ | $H_2$ | $CO_2$ | CO | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.67 | 0.33 | 0.00 | 0.00 | 0.00 | 38 | 2:1 | 57 | 0.0013 | 21 | 48 | 1.3 | 1.5 | 12 |
| 2 | 0.60 | 0.30 | 0.04 | 0.03 | 0.03 | 49 | 2:1 | 60 | 0.0012 | 26 | 61 | 2.0 | 1.1 | 9 |
| 3 | 0.53 | 0.27 | 0.08 | 0.06 | 0.05 | 52 | 2:1 | 70 | 0.0010 | 30 | 75 | 1.3 | 0.6 | 7 |

[a] Power = 118 W, frequency = 174 Hz, water temperature in water jacket = 28 °C.

**Table 4. Staged Reactors in Series Experimental Results[a]**

| stage | feed mole fraction | | | | | % C selectivity (mole basis)[b] | | | | | | | |
| | $CH_4$ | $O_2$ | $H_2$ | $CO_2$ | CO | $CO_2$ | CO | E | M | MF | FA | F | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.67 | 0.33 | 0.00 | 0.00 | 0.00 | 16 | 18 | 2 | 17 | 9 | 25 | 15 | 102 |
| 2 | 0.60 | 0.30 | 0.04 | 0.03 | 0.03 | 18 | 10 | 2 | 14 | 8 | 21 | 17 | 90 |
| 3 | 0.53 | 0.27 | 0.08 | 0.06 | 0.05 | 22 | 10 | 3 | 10 | 11 | 14 | 13 | 83 |

[a] Power = 118 W, frequency = 174 Hz, water temperature in water jacket = 28 °C. [b] E = ethane, M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, S = sum of carbon selectivity.

**Table 5. Recycle Experimental Results[a]**

| recycle ratio | moles of $CH_4$ conv. (mol/min) | eV per molecule of $CH_4$ conv. | mol % $CH_4$ conv. | mol % $CH_4$ conv. per pass | mol % $O_2$ conv. | $H_2/CO$ | $H2/CO_2$ | $H_2$ Sel. | % C selectivity (mole basis)[b] | | | | | | | | | |
| | | | | | | | | | $CO_2$ | CO | E | Pr | $n$-B | M | MF | FA | F | El | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.0005 | 138 | 46 | 46 | 100 | 2.9 | 4.4 | 28 | 13 | 19 | 13 | 3 | 1 | 6 | 8 | 19 | 11 | 1 | 94 |
| 160 | 0.0006 | 129 | 49 | .6 | 100 | 2.9 | 2.2 | 16 | 15 | 11 | 4 | 0 | 0 | 17 | 5 | 12 | 10 | 7 | 81 |

[a] Power = 118 W, frequency = 174 Hz, water temperature in water jacket = 28 °C, $CH_4/O_2$ flow rate input ratio = 2.5:1. [b] E = ethane, Pr = propane, $n$-B = $n$-butane, M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, El = , S = sum of carbon selectivity.

The second reason for decreased energy efficiency is that, as the partial pressures of carbon monoxide, carbon dioxide, and hydrogen build from one stage to the next, the probability of oxygen reacting with methane decreases. However, because carbon monoxide, carbon dioxide, and hydrogen can react with other gas species in the reaction zone, they cannot be regarded only as diluents. The results also show that the oxygen conversion increased by 36% because the residence time increased by 27% from stage one to stage three as the flow rate decreased. Thus, oxygen has more time to be converted when going from one stage to the next. Furthermore, the results show that the CO selectivity decreased by 44%, whereas the $CO_2$ selectivity increased by 27% from stage one to stage three. The 44% drop in CO selectivity is a result of the CO formed in previous stages being overoxidized to $CO_2$. Finally, there was a 30% decrease in the molar rate of organic oxygenate species production from stage one to three because there was less oxygen and methane in stage three available to form organic oxygenate species. However, the overall organic oxygenate yield of this system was 35%. This is significant because, although much research has been done in the area of methane conversion, the yields of organic liquid products, such as methanol, have not been that high in one-step processes.[15−17]

**Recycle Experiments.** The next experiments examine the changes that occur in the partial oxidation of methane when recycle operation at a high recycle ratio is used with a short per-pass residence time. The first experiment of this series has a $CH_4/O_2$ feed ratio of 2.5:1 and a feed flow rate of 40 $cm^3$/min to the system. The power and frequency are 118 W and 174 Hz, respectively. The system pressure is 1 atm, and the water temperature in the water jacket is 28 °C. This experiment has no recycle stream. The second experiment is identical to the first, except that a pump is placed downstream of the liquid traps. The liquid traps, which condense the organic oxygenates, are directly down-

stream of the reactor outlet. The pump recycles 3590 $cm^3$/min of gas product stream. This recycle stream then combines with the 40 $cm^3$/min 2.5:1 $CH_4/O_2$ system feed stream, and the combined stream is fed to the reactor. These conditions give a per-pass residence time of 2.3 s. A gas stream purge, located after the traps, flows to the Carle GC for analysis.

Table 5 compares the partial oxidation of methane occurring in the silent electric discharge reactor both with and without recycle. The methane conversion showed little change between the recycle and the nonrecycle experiments, despite better gas mixing in the recycle experiment. In both experiments, the oxygen conversion was 100%, but the nonrecycle experiment was 69% higher in ethane selectivity when compared to the recycle experiment. In addition, the nonrecycle experiment had a 4% overall selectivity for propane and $n$-butane, whereas the recycle experiment showed no selectivity toward these compounds. The reason for these differences is that the high recycle ratio in the recycle experiment causes the gases within the reactor to be well-mixed and, therefore, increases the probability of ethane reacting with oxygen and forming ethanol. This can be seen in the ethanol selectivity, which is 1% in the nonrecycle experiment compared to 7% in the recycle experiment. In the nonrecycle experiment, however, the gases within the reactor are near plug-flow conditions. Thus, as the ethane partial pressure increased to a significant amount, the oxygen partial pressure was already extremely limited or zero. This meant that ethane reacted with ethane and methane molecules to form $n$-butane and propane, respectively. This chain-building behavior has been studied by Caldwell et al.[12] Finally, the sum of organic oxygenate products was 12% higher, whereas the $CO_x$ selectivity was 19% lower in the recycle experiment. Because the methane conversion per pass in the recycle experiment was only 0.6%, because of very low residence times per pass, the low partial pressures of the organic

**Table 6. Nitrogen Experimental Results**[a]

| feed mole fraction (mol %) | | | moles of CH$_4$ conv. (mol/min) | eV per molecule of CH$_4$ conv. | mol % CH$_4$ conv. | mol % O$_2$ conv. | H$_2$/CO | H2/CO2 |
|---|---|---|---|---|---|---|---|---|
| CH$_4$ + O$_2$ (CH$_4$/O$_2$ = 2:1) | N$_2$ | N$_2$/O$_2$ | | | | | | |
| 100 | 0 | 0 | 0.0014 | 51 | 12 | 26 | 1.1 | 1.6 |
| 90 | 10 | 0.3 | 0.0014 | 52 | 13 | 29 | 1.2 | 1.5 |
| 80 | 20 | 0.8 | 0.0012 | 63 | 12 | 24 | 1.1 | 1.5 |
| 70 | 30 | 1.3 | 0.0010 | 70 | 13 | 33 | 1.0 | 1.5 |
| 60 | 40 | 2 | 0.0011 | 66 | 16 | 39 | 1.1 | 1.5 |

[a] Power = 118 W, frequency = 174 Hz, water temperature in water jacket = 28 °C, residence time = 20 s.

**Table 7. Nitrogen Experimental Results**[a]

| feed mole fraction (mol %) | % C selectivity (mole basis)[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CH$_4$ + O$_2$ (CH$_4$/O$_2$ = 2:1) | N$_2$ | CO$_2$ | CO | E | M | MF | FA | F | org. liq. sum | S |
| 100 | 0 | 13 | 19 | 2 | 16 | 9 | 17 | 12 | 54 | 88 |
| 90 | 10 | 16 | 20 | 2 | 11 | 17 | 14 | 9 | 51 | 89 |
| 80 | 20 | 17 | 23 | 2 | 14 | 19 | 19 | 12 | 64 | 106 |
| 70 | 30 | 18 | 27 | 2 | 11 | 12 | 19 | 11 | 53 | 100 |
| 60 | 40 | 18 | 26 | 2 | 10 | 12 | 20 | 9 | 51 | 97 |

[a] Power = 118 W, frequency = 174 Hz, water temperature in water jacket = 28 °C, residence time = 20 s. [b] E = ethane, M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, S = sum of carbon selectivity.

oxygenate species did not permit these products to be condensed in the reactor at 28 °C, but they were able to be condensed in the liquid trap at −55 °C. Thus, using a recycle at high recycle ratios with a low-temperature liquid trap minimizes the organic oxygenates' chances of becoming overoxidized and, therefore, increases their yield while decreasing CO$_x$ production. Finally, even at the high recycle ratio, the CO$_x$ selectivity was still 26%. This, therefore, suggests that there is a parallel direct oxidative pathway between CH$_4$ and CO$_x$.

**Nitrogen Experiments.** The next series of experiments examines the effect of nitrogen on the partial oxidation of methane in the DBD reactor. In all of these experiments, the total feed flow rate is 430 cm$^3$/min to give a residence time of 20 s, and the CH$_4$/O$_2$ feed ratio is kept constant at 2:1. The power and frequency are set at 118 W and 174 Hz, respectively. The water temperature in the water jacket is 28 °C, and the system pressure is 1 atm. The concentration of nitrogen in the feed is varied from 0 to 40 mol %.

Tables 6 and 7 show the results of the methane−oxygen−nitrogen experiments. The results show that as the N$_2$/O$_2$ ratio went from 0:1 to 2:1, the rate of methane converted went from 0.0014 to 0.0011 mol/min, which in turn caused the energy efficiency to decrease by 23%. This occurred because N$_2$ was acting as a diluent as it was virtually nonreactive in the reaction zone. The CO and CO$_2$ selectivities increased by 27 and 28%, respectively, when the N$_2$/O$_2$ ratio was changed from 0:1 to 2:1, although the organic oxygenate liquid sum did not decrease, as would be expected with overoxidation of these products.

**Methane−Ethane−Oxygen Experiments.** The final series of experiments examines methane−ethane−oxygen systems. In all but one of the experiments, the hydrocarbon-to-oxygen feed ratio is 2:1. The one exception is the experiment that has only ethane and a C$_2$H$_6$/O$_2$ feed ratio of 1.8:1. All of the experiments have a total feed flow rate of 430 cm$^3$/min. The power and frequency are kept at 118 W and 174 Hz, respectively. The water temperature in the water jacket in all of the experi-

ments is 28 °C. In these experiments, the CH$_4$/C$_2$H$_6$ feed ratio is varied from 14.6:1 to 1:1. Three other experiments consist of a methane−oxygen experiment with a CH$_4$/O$_2$ feed ratio of 2:1, an ethane−oxygen experiment with a C$_2$H$_6$/O$_2$ feed ratio of 2:1, and an ethane−oxygen experiment with a C$_2$H$_6$/O$_2$ feed ratio of 1.8:1.

Table 8 shows the methane−ethane−oxygen experimental results. The results show that the energy efficiency increased by 49% for the 2:1 C$_2$H$_6$/O$_2$ feed, compared to that for the 2:1 CH$_4$/O$_2$ feed. Although their conversions are the same, for every 1 mol of ethane reacting, 2 mol of carbon are converted, whereas for each mole of methane reacting, only 1 mol of carbon is converted. This result shows that, even though the bond energy in a carbon−carbon bond in ethane is 16% less than the carbon−hydrogen bond energy in methane, the ethane conversion is not enhanced compared to the methane conversion. The energy efficiency for the ethane−oxygen system was further increased by 12% by lowering the 2:1 C$_2$H$_6$/O$_2$ ratio to 1.8:1. This is also due to the enhancement of the reaction rate by oxygen.

The liquid selectivities of quantified organic oxygenate liquid compounds decreased when the feed was changed from a 2:1 CH$_4$/O$_2$ mixture to a 2:1 C$_2$H$_6$/O$_2$ mixture. The exception to this trend was ethanol's selectivity, which increased and can account for 9−13% of the ethane reacted. Three identified (acetaldehyde, ethyl formate, and acetic acid) but not quantified organic oxygenate liquid products also substantially increased in selectivity when the ethane partial pressure in the feed increased. This was determined by the fact that their integrated areas in the Varian GC analysis increased with increasing partial pressure of ethane. The sum of these three products' areas accounted for 33% of the total organic liquid area in the 2:1 ethane/oxygen experiment. Evidently, ethane is reacting with oxygen and forming C$_2$ and C$_2$+ organic oxygenate species.

The CO$_x$ selectivity decreased by 50% when the feed stream was changed from a 2:1 CH$_4$/O$_2$ mixture to a 2:1 C$_2$H$_6$/O$_2$ mixture. The reason for this decrease in CO$_x$ is uncertain. Potentially, this is because the additional organic oxygenates that formed due to ethane chemistry (ethanol, acetaldehyde, ethyl formate, and acetic acid) have higher dew points than their corresponding organic oxygenate counterparts that are traditionally formed due to methane chemistry (methanol, formaldehyde, methyl formate, and formic acid). Thus, the fraction of organic oxygenates in the liquid phase might be higher, which decreases the chances of overoxidation. Ethane−oxygen experiments at a high recycle ratio might also provide further insight into whether there is a direct oxidative pathway from ethane to CO$_x$ and how significant it is. At this point with the present experiments, it is difficult to determine what relationship exists

**Table 8. Methane−Ethane−Oxygen Experimental Results[a]**

| feed mole fraction | | | moles of C conv. (mol/min) | eV per atom of C conv. | mol % $CH_3CH_3$ conv. | mol % $CH_4$ conv. | mol % $O_2$ conv. | % C selectivity (mole basis)[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | E | $O_2$ | | | | | | $CO_2$ | CO | E | M | MF | FA | F | El | S[c] |
| 0.67 | 0.00 | 0.33 | 0.0014 | 51 | 0 | 12 | 26 | 13 | 19 | 2 | 16 | 9 | 17 | 12 | 0 | 88 |
| 0.64 | 0.04 | 0.31 | 0.0018 | 41 | 36 | 11 | 30 | 13 | 14 | | 13 | 5 | 14 | 12 | 3 | 74 |
| 0.47 | 0.20 | 0.33 | 0.0026 | 28 | 25 | 10 | 31 | 10 | 9 | | 8 | 3 | 9 | 10 | 6 | 55 |
| 0.33 | 0.33 | 0.33 | 0.0025 | 29 | 19 | 6 | 30 | 9 | 9 | | 8 | 3 | 11 | 11 | 10 | 61 |
| 0.00 | 0.67 | 0.33 | 0.0028 | 26 | 12 | 0 | 26 | 8 | 8 | | 5 | 2 | 7 | 8 | 13 | 51 |
| 0.00 | 0.64 | 0.36 | 0.0032 | 23 | 14 | 0 | 27 | 8 | 6 | | 5 | 1 | 8 | 8 | 13 | 49 |

[a] Power = 118 W, frequency = 174 Hz, residence time = 20 s, water temperature in water jacket = 28 °C. [b] E = ethane, M = methanol, MF = methyl formate, FA = formic acid, F = formaldehyde, El = ethanol, S = sum of carbon selectivity. [c] Acetaldehyde, ethyl formate, and acetic acid have been detected but not quantified. They account for 33% of the total TCD GC area count of the organic oxygenate products for the 2:1 ethane−oxygen system.

between methane and ethane in the methane−ethane−oxygen experiments because the observed methane−ethane conversions might not accurately represent the actual conversions because of interconversion between the two.[12]

## Conclusions

Previous work has shown that decreasing the oxygen partial pressure in a methane−oxygen feed for a silent electric discharge reactor decreased the methane conversion rate.[8] With this in mind, the energy efficiency experimental results of this work showed that, when the gap distance, methane−oxygen feed ratio, and system pressure were fixed in the partial oxidation of methane in a silent electric discharge reactor, the energy efficiency of the system was determined by the partial pressure of oxygen within the reactor.

The hydrogen experimental results showed that increasing the partial pressure of hydrogen in a methane−oxygen−hydrogen experiment increased the $CO_2$ selectivity with little change in the CO selectivity. In addition, the net rate of hydrogen destruction was greater than the net rate of hydrogen creation. This indicates that hydrogen was reacting with oxygen to form water and that the water-gas shift reaction was a secondary reaction.

The energy efficiency of methane−oxygen−hydrogen systems as well as methane−oxygen−nitrogen systems, was affected by both the partial pressure of hydrogen (or nitrogen) and the partial pressure of oxygen when the methane oxygen feed ratio was fixed. Increasing the hydrogen (or nitrogen) partial pressure in the feed decreased the probability of methane colliding and then reacting with an active oxygen species. In the case of hydrogen, the probability was even further decreased because hydrogen was evidently reacting with oxygen and forming water.

The staged reactors-in-series experimental results showed that decreasing the partial pressures of oxygen and methane and increasing the partial pressures of CO, $CO_2$, and $H_2$ in the feed decreased the energy efficiency and organic oxygenate production.

The recycle experimental results showed that organic oxygenate liquid production can be enhanced while $CO_x$ production is minimized through the use of high recycle ratios. In addition, CO and $CO_2$ were still present in the high recycle ratio experiment, suggesting a direct oxidation pathway from $CH_4$ to CO and $CO_2$.

Replacing methane with ethane in an oxygen-rich feed stream did not show an increase in conversion in ethane, but the number of electronvolts per atom of carbon converted was about halved.

The current large-scale industrial process for methanol production, steam reforming of methane to synthesis gas followed by methanol synthesis, requires about 11 eV per molecule of methanol produced.[18] However, at a remote natural gas site the efficiency of this process would probably be lower because the plant size would have to be scaled down because of the limited gas reserves. The best result obtained in this work is 51 eV per molecule of methane converted with a 13% selectivity of $CO_2$. Thus, the system consumes 59 eV per molecule of usable carbon products, which is less efficient than the industrial methanol synthesis process. However, this might not represent the true difference between the two processes because they are scaled to different sizes (large industrial scale vs bench scale). Both processes would have to be of similar scale for a fair comparison to be made.

High methane conversions can be obtained in the silent electric discharge reactor, but at the expense of energy efficiency. This problem can be lessened by having staged reactors in series with intermediate oxygen addition, which allows for high methane conversions with better energy efficiency. In fact, the staged experiments also produced a 35% liquid oxygenate yield, the best results to date.

## Acknowledgment

## Literature Cited

(1) Lange, J.-P. Perspectives for Manufacturing Methanol at Fuel Value. *Ind. Eng. Chem. Res.* **1997**, *36*, 4282−4290.

(2) Tas, M. A. Plasma-Induced Catalysis: A Feasibility Study and Fundamentals. Ph.D. Thesis, Eindhoven University of Technolgy, Eindhoven, The Netherlands, 1995.

(3) Chang, J. S.; Lawless, P. A.; Yamamoto, I. *IEEE Trans. Plasma Sci.* **1991**, *19* (6), 1152−1164.

(4) Eliasson, B.; Kogelschatz, U. Nonequilibrium Volume Plasma Chemical Processing. *IEEE Trans. Plasma Sci.* **1991**, *19* (6), 1063−1077.

(5) Bruno, G.; Capezzuto, P.; Cicala, G. *Chemistry of Amorphous Silicon Deposition Processes: Fundamentals and Controversial Aspects*; Academic Press: Boston, MA, 1995.

(6) Zhou, L. M.; Xue, B.; Kogelschatz; U.; Eliasson, B. Partial Oxidation of Methane to Methanol with Oxygen or Air in a Nonequilibrium Discharge Plasma. *Plasma Chem. Plasma Process.* **1998**, *18* (3), 375−393.

(7) Yao, S.; Takemoto, T.; Ouyang, F.; Nakayama, A.; Suzuki, E. Selective Oxidation of Methane Using a Non-Thermal Pulsed Plasma. *Energy Fuels* **2000**, *14* (2), 459−463.

(8) Bhatnagar, Rajat, Mallinson, R. G. Methane Conversion in AC Electric Discharges at Ambient Conditions. *Methane and Alkane Conversion Chemistry*; Plenum Press: New York, 1995; pp 249−264.

(9) Bhatnagar, R. A Study of the Partial Oxidation of Methane Under the Influence of an AC Electric Discharge. M. S. Thesis, University of Oklahoma, Norman, OK, 1993.

(10) Larkin, D. W.; Caldwell, T. A.; Lobban, L. L.; Mallinson, R. G. Oxygen Pathways and Carbon Dioxide Utilization in Methane Partial Oxidation in Ambient Temperature Electric Discharges. *Energy Fuels* **1998**, *12* (4), 740−744.

(11) Larkin, D. W.; Leethochawalit, S.; Caldwell, T. A.; Lobban, L. L.; Mallinson, R. G. Carbon Pathways, $CO_2$ Utilizaton, and In Situ Product Removal in Low Temperature Plasma Methane Conversion to Methanol. *Greenhouse Gas Control Technologies*; Elsevier Science Ltd.: New York, 1999; pp 397−402.

(12) Caldwell, T. A.; Poonphatanaricha, P.; Chavadej, S.; Mallinson, R. G.; Lobban, L. L. Third-Body Enhanced Methane Conversion In a Dielectric-Barrier Discharge Reactor. ACS National Meeting, Aug 1998, Boston, MA.

(13) McMurry, J. *Organic Chemistry*, 2nd ed.; Brooks/Cole Publishing Company: Pacific Grova, CA, 1988.

(14) Eliasson, B.; Egli, W.; Kogelschatz, U. Modeling of Dielectric Barrier Discharge Chemistry. *Pure Appl. Chem.* **1994**, *66* (6), 1275−1286.

(15) Hunter, N. R.; Gesser, H. D.; Morton, L. A.; Yarlagadda, P. S. Methanol Formation at High Pressure. *Appl. Catal.* **1990**, *57*, 45−54.

(16) Rytz, D. W.; Baiker, A. Partial Oxidation of Methane to Methanol in a Flow Reactor at Elevated Pressure. *Ind. Eng. Chem. Res.* **1991**, *30*, 2287−2292.

(17) Foulds, G. A.; Gray, B. F. Homogeneous Gas-Phase Partial Oxidation of Methane to Methanol and Formaldehyde. *Fuel Process. Technol.* **1995**, *42*, 129−150.

(18) Rostrup-Nielson, J. R. Catalysis and Large-Scale Conversion of Natural Gas. *Catal. Today* **1994**, *21*, 257−267.