

CARBON PATHWAYS, CO₂ UTILIZATION, AND *IN SITU* PRODUCT REMOVAL IN LOW TEMPERATURE PLASMA METHANE CONVERSION TO METHANOL

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ABSTRACT

This study examines a non-equilibrium "cold" plasma reaction system for the partial oxidation of methane as well as the water-gas shift reaction and CO₂ reforming of methane. Cylindrical and planar plasma reactors are used. Both systems have a glass dielectric interposed between two metal electrodes. The electrodes are supplied with kV ac power with frequencies ranging from 50 Hz to 100 Hz. The results show that lowering the reaction temperature from 75 °C to 28 °C in the partial oxidation experiments increases overall organic oxygenate liquid selectivities from 24% to 52%. The lower temperatures reduce these products' vapor pressures to their equilibrium partial pressures allowing condensation within the reactor. Experiments involving CO and H₂O, and CO₂ and H₂ confirm that the water-gas shift reaction pathway occurs along with the partial oxidation of methane. Results of carbon dioxide reforming of methane indicates that the CO₂:CH₄ ratio strongly affects the results. The ethane and hydrogen selectivity decrease when the CO₂:CH₄ ratio is reduced from 1:2 to 1:1. This decrease in partial pressure of methane decreases direct coupling to ethane. Increasing the partial pressure of CO₂ from a 1:2 to 1:1 CO₂:CH₄ ratio causes increased CO₂ conversion to CO. The selectivity for methanol under reforming conditions is less than 1%. A further increase in the CO₂:CH₄ ratio from a 1:1 to 2:1 causes an increase in ethane and hydrogen selectivity indicating that an oxidative coupling pathway may play a role under these conditions. Finally, the results show that the presence of helium enhances methane conversion and alters the reaction selectivities despite lowering methane partial pressures, thus indicating a third body effect on methane activation.

INTRODUCTION

Presently, natural gas is being used as a combustion fuel in industrialized areas that are close to large natural gas reserves. Steam reforming and further conversion to methanol is a major process that utilizes natural gas for its chemical value. This commercial technology is a complex multi-step process which is energy intensive.

There is also a considerable amount of natural gas in "remote" areas around the world. Many of these natural gas reserves cannot be utilized presently due to high transportation costs. This problem could be reduced if those resources could be processed into organic liquids, such as methanol, that did not need refrigeration or compression for transport.¹

One technique that could prove to be a favorable alternative technology is the direct partial oxidation of methane to methanol. Methanol is currently being used as a feed stock to manufacture formaldehyde and methyl tert-butyl ether, among other uses. The chemical market for methanol is only 24 million tons per year which is far less than the estimated 107 million tons of natural gas reserves. Multi-step processes such as steam reforming and then synthesis are too expensive to implement for remote locations or for fuel value, rather than chemical value. Thus, a one-step partial oxidation process which substantially reduces the processing cost could allow effective utilization of these gas reserves.²

Currently, there is no one-step partial oxidation process that is economically feasible. Plasma reactors may provide a useful technology for solving this problem. These types of reactors are already being used to study different possible applications in control of NO_x, SO_x, toxic gases, volatile organic compounds, hazardous emissions, and for ozone synthesis. The plasmas these reactors create can be equilibrium or non-equilibrium plasmas. A plasma is in equilibrium when the kinetic energy of the charged particles and neutral species are the same. Non-equilibrium plasmas are plasmas in which the electrons have a much higher kinetic energy than the ions and neutral species. For example, applying strong electric fields at appropriate pressures can generate electron energies in the range of 1 to 10 eV while the rest of the molecules' energies are a few hundredths of an eV. These nonequilibrium plasmas can be created at ambient temperature by discharge systems, such as the silent electric discharge, and can induce significant chemical reactions.^{3,4}

This study uses a silent electric discharge reactor to generate a non-equilibrium plasma which causes the direct partial oxidation of methane. The reactor operates at near ambient temperatures and atmospheric pressure. Planar and cylindrical geometries with about the same volume and gap distance are used in this study. A comparison of their performance is made when processing identical 3:1 CH₄:O₂ feeds with the same 1 minute residence time.

The effect of reactor wall temperature is investigated in this study to determine if lowering the reactor temperature increases liquid organic oxygenate production while decreasing CO_x production in the partial oxidation of methane. Lowering the reaction temperature lowers the vapor pressures of the "liquid" oxygenate products and, thus,

causes more of these desirable products to be condensed *in-situ*. This decreases their chances of being over-oxidized since they are no longer in the gas phase reaction zone.

In partial oxidation experiments, shown in previous work, the rate of destruction of CO₂ was found to be greater than the rate of creation of CO₂ when the CO₂ partial pressure was significant.¹ This paper studies the role of the water-gas shift reaction (and its reverse) in CO₂ production and destruction in the partial oxidation system.

Also in this study, the utilization of carbon dioxide in carbon dioxide reforming of methane is examined. The use of CO₂ for reforming may reduce net CO₂ production when synthesis gas (or hydrogen) is produced. Additionally, since CO₂ is present in many natural gas resources, its ability to be tolerated and even enhance partial oxidation is of interest.

EXPERIMENTAL SECTION

The feed gas system uses mass flow controllers, (Porter Instrument Company) to regulate the flow rates of these gases. The feed gas enters the plasma reactor at the top. Both cylindrical and planar geometries are used. The cylindrical reactor is used in the partial oxidation, water-gas shift, and temperature experiments. It consists of two concentric cylinders with a glass inner cylinder with a metal foil on its inside acting as one electrode while the outer stainless steel wall acts as the other electrode. The outer stainless steel cylinder and inner glass tube are separated by a gap through which gases flow axially. Thus, the reactor acts like a capacitor with the glass as the dielectric. This type of discharge has electrons crossing the gap in "micro-discharge" streams which are relatively uniformly dispersed throughout the volume between the electrodes. From exterior to interior the reactor layers comprise a water jacket, outer stainless steel electrode, gas gap, glass plate, and inner stainless steel electrode. The products exit the reactor from the bottom. The gap that the gas flows through is a 0.27 cm wide annular space. The active reaction area is 920 cm² and the effective annular volume of the reactor is 225 milliliters.

The reactor product stream is fed through a trap cooled by dry ice and acetone which is at -40 °C. Methanol, methyl formate, formic acid, ethanol, formaldehyde, and water are collected. Depending on reactor temperature, these products may condense in the reactor and be carried out by the gas stream. The remaining gas effluent stream is fed to an EG&G Carle Series 400 AGC gas chromatograph. Appropriate columns are used to analyze the hydrocarbons, CO_x species, oxygen, and hydrogen which are the remaining components of the gas stream. The flow rate of the gas stream is determined by using a soap bubble flow meter. The calibrations for all the gases are on an absolute basis. The liquid products are analyzed with a Varian 3300 GC which contains a Porapak Q column.

A planar plasma reactor is used in the partial oxidation of methane and the CO₂ methane reforming experiments. Two flat aluminum plates are used as the electrodes for this reactor. Between the top and bottom aluminum plates is a glass dielectric and a teflon spacer which creates the volume for the gas flow. The electrode without the glass dielectric has a water jacket on its exterior side. In the partial oxidation experiments, the gas gap and reactor volume are .25 cm and 200 cm³, respectively. These dimensions are very similar to the cylindrical reactor system but the design allows for variation of reactor geometry. The reactor volume in the CO₂ reforming experiments is 216 cm³. For the partial oxidation experiments, the system used in the collection and analysis of the products is the same as that used in the cylindrical reactor. The gases in the CO₂ reforming of methane experiments, however, are analyzed by a Perkin-Elmer "Autosystem" Gas Chromatography apparatus which has both TCD and FID detectors. Haysep DB and T columns are used to separate the methane, CO₂, CO, acetylene, ethylene, ethane, hydrogen, and methanol.

For both reactor systems, the AC power supply is an Elgar model 501SL. A CBK Precision function generator is used in conjunction with the power supply to form a sinusoidal waveform at the desired frequency which is stepped up by 125 times through the use of a transformer and is then supplied to the reactor.

In the CO₂ reforming experiments, a variable transformer is used to vary the primary voltage from 0 to 110 volts with the use of 220 V AC line voltage at a fixed frequency of 50 Hz. A high voltage transformer then steps up the voltage by a factor of 125 times. The output of the high voltage transformer is then supplied to the reactor.

In the first series of experiments, the cylindrical reactor performance is compared with the planar reactor system. For these experiments, the residence time is one minute and the CH₄:O₂ ratio is kept constant at 3:1. The difference in power used by the two reactors for these experiments is 15%.

Experiments to examine the effect of *in-situ* product condensation on product selectivities used the cylindrical reactor. Methane and oxygen are fed to the reactor at a ratio of 3:1 with a total flow rate of 200 cc/min. This gives a residence time of 1 minute. The frequency and voltage are set at 100 Hz and 7.6 kV, respectively. The experimental variable for the four experiments conducted is the water jacket temperature.

In the next series of experiments the reverse water-gas shift reaction is studied by feeding hydrogen and carbon dioxide to the cylindrical reactor. The H₂:CO₂ ratios used are 3:1, 4:1, 5:1, and 6:1. For all four experiments the residence time is 2 minutes. The frequency and voltage are 87 Hz and 5.9 kV, respectively. The water temperature in the water jacket is maintained at 15 degrees C.

The water-gas shift reaction is studied by feeding CO and H₂O to the cylindrical reactor. Carbon monoxide is bubbled through a flask of water at 57.8 degrees C. This provides an inlet mole fraction of water of 0.18 based upon saturation calculations. The water in the water jacket for this experiment is set at 80 degrees C. Thus, water fed to the

reactor should be retained in the vapor phase. The residence time is 2 minutes. The frequency and voltage are 90 Hz and 7 kV, respectively.

In the first series of methane reforming experiments, the $\text{CO}_2:\text{CH}_4$ ratio is varied from pure methane, 1:2, 1:1, and 2:1. For each $\text{CH}_4:\text{CO}_2$ ratio, the experiment is repeated at voltages of 5.5 kV, 6.6 kV, and 7.7 kV. For all of these experiments, the space time is 4 minutes and 80% of the feed is helium.

In the next series of experiments the helium concentration is varied with the balance of the feed gas being CH_4 and CO_2 at a 1:1 ratio. For a given helium concentration the experiment is conducted with four minute and six minute space times. For each space time the voltage is also varied from 5.5 kV to 7.7 kV.

RESULTS AND DISCUSSION

The results of the partial oxidation experiments in the cylindrical and planar reactors are shown in Tables 1 and 2. The plasma reactors operate at the same 1 min. residence time and within 15 % of the power of one another. The cylindrical reactor has a gap thickness of .27 cm while the planar reactor's gap thickness is .25 cm. Comparing the two systems, it can be seen that the methane and oxygen conversions are within 4% and 10% of one another, respectively. The only significant difference comes in formaldehyde selectivity in which the planar system has a much lower selectivity for it. Thus, the different reactor geometries produce generally similar results.

The results obtained for partial oxidation and water-gas shift (and its reverse) experiments, presented in Tables 3-6, are carried out in the cylindrical reactor. Tables 3-4 show the partial oxidation results when the reactor wall temperature is varied. The results show that changes in water jacket temperature from 6 to 75 degrees C, results in only small changes in methane conversion, while oxygen conversion increased significantly from 67% to 88%. The ethane selectivity remains relatively constant with increasing temperature but the CO and CO_2 selectivities both increase. The "liquid" selectivities, except for methyl formate and ethanol, which shows little change, generally decrease with increasing temperature. Thus, as can be seen in the last two columns of Table 3, the overall trend for increasing water jacket temperature is that the sum of the "liquid" selectivities decreases while the sum of the "gas" selectivities increase. The increased selectivities for CO_x at higher temperatures due to "over" oxidation of the "liquid" products is consistent with higher oxygen conversion with little change in methane conversion. Because the reactor operates at such low temperatures, as the methane conversion increases as the gases pass along the length of the reactor, the partial pressures of the products increase. The partial pressures of the heavier "liquid" components reach their vapor pressures at sufficiently low temperatures that condensation on the cooled wall occurs. Thus, under ideal conditions, the low temperatures achievable in these reactors result in low partial pressures of these products in the gas phase, thus minimizing their availability to be further oxidized to "gas" products, CO_x .

Table 4 shows that the power and eV per molecule of converted CH_4 for these experiments increase 17% and 9.4%, respectively, as the temperature increases from 6 to 75 degrees C. The change in eV per molecule is primarily the result of the significant change in the power used. Thus at the lower temperatures, not only are more liquid products being recovered, but energy efficiency is higher.

The results of the water-gas shift reaction experiments are shown in Table 5. The only two products observed in any of the four experiments are CO and water. As shown in the table, increasing partial pressure of hydrogen results in decreased hydrogen conversion while CO_2 conversion increases. An increase in partial pressure of hydrogen also results in an increase in the eV/molecule of converted CO_2 . Table 6 shows the results of having CO and H_2O as the feed gas where the products are hydrogen and CO_2 , as expected. The $\text{H}_2:\text{CO}_2$ ratio of the products is 1:2 which suggests that half of the O atoms combining with CO to form CO_2 came from CO. These results demonstrate that the water-gas shift reaction pathway occurs in these systems. These results also indicate that when CO and CO_2 are present in methane partial oxidation, a balance between CO and H_2 production is established. Thus, CO_2 production can be minimized or eliminated, as shown in previous work, while producing a synthesis gas that could be used for methanol production.

The results for the first series of CO_2 reforming experiments, as outlined in the experimental section, can be seen in Tables 7-9. As may be seen in all three tables, an increase in voltage increases the conversion. These results also generally indicate that as the $\text{CO}_2:\text{CH}_4$ ratio increases, the methane conversion becomes greater as can be seen most clearly in Table 9 at 7.7 kV. In previous work with the cylindrical reactor, the methane conversion in pure methane was about 3 %. For the same residence time, frequency, and voltage with a 3:1 methane to oxygen feed, the methane conversion was 14 %. The methane conversion in the 2:1 $\text{CO}_2:\text{CH}_4$ (at 7.7 kV) is intermediate to these other two cases. The lower conversions in the experiments with CO_2 compared with the experiments with molecular oxygen present, suggest that an active oxygen species helps initiate the conversion of methane which CO_2 is not capable of producing in the same quantity, if at all. One simple explanation for this result is that the bond strength of the $\text{O}=\text{O}$ bond is 495 kJ/mol compared to the $\text{C}=\text{O}$ bond in CO_2 which is 799 kJ/mol. Therefore, a more energetic process may be required to "abstract" an oxygen atom from CO_2 than O_2 , though there is no evidence in this study of the important active species in these different systems.

The highest fractional conversion of CO_2 occurs at a 1:2 $\text{CO}_2:\text{CH}_4$ ratio. The fractional conversion for the 1:1 and 2:1 ratios of $\text{CO}_2:\text{CH}_4$ is lower than 1:2, but fairly similar with each other at the same voltage. Once again, for all the experiments, an increase in voltage increases CO_2 conversion for a given feed ratio.

The selectivity for ethane is also shown in Tables 7-9. In these experiments at least 98% of the C₂ products formed is ethane. The highest selectivity for ethane occurred with pure methane as the feed where the only initially observable products are C₂ species and H₂. With a CO₂:CH₄ ratio of 1:1, ethane selectivity is lower, presumably due to the lower partial pressure of CH₄, and a decreased rate of direct methane coupling is observed. At the higher CO₂ ratio of 2:1 CO₂:CH₄, ethane selectivity is higher than for the 1:1 experiments. This is consistent at all the voltages and space times. These results suggest that while direct methane coupling is a major pathway in ethane formation, an oxidative pathway may play a role at higher CO₂ partial pressures.

The hydrogen selectivity in these experiments appears to be related to ethane production because hydrogen is produced in the methane coupling reaction.

Carbon monoxide is the other major carbon product in these experiments. Until experiments with isotopically labeled CO₂ are conducted, it can not be established how much of the CO comes from methane under these conditions. In partial oxidation experiments when neither CO or CO₂ is present in the feed, CO is clearly produced from methane.

The effect of adding helium to a 1:1 CO₂:CH₄ ratio feed stream was studied in a series of experiments conducted at 5.5, 6.6, and 7.7 kV with 4 minute and 6 minute space times. Table 10 shows the results for 5.5 kV and a 4 minute space time. All the experiments show the same trends, though some are not as uniform as those in Table 10. In these experiments, as the helium partial pressure is increased the methane conversion increases despite lower partial pressures of the reactant gases. When the helium partial pressure is increased, ethane selectivity decreases, but the carbon monoxide selectivity increases. These experiments suggest that helium may contribute third body reactions in methane conversion, rather than act just as a diluent. The decrease in ethane selectivity with higher methane conversion may simply be due to the dilution of the second order coupling reaction.

Table 1: 3:1 CH₄:O₂, 1 min. residence time(Reactor type: p= planar, c = cylindrical)

Geometry & gap d. (cm)	Mole % CH ₄ Conv.	Mole % O ₂ Conv.	% Ethane Select.	% CO Select.	% CO ₂ Select.	% Me Select.	% MF Select.	% FA Select.	% F Select.	% Et Select.	Org. Liquid Sum
.27 (c)	24	74	4	14	13	17	5	16	13	1	52
.25 (p)	25	82	5	18	15	23	8	22	2	0	55

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

Table 2: 3:1 CH₄:O₂, 1 min. residence time(Reactor type: p = planar, c = cylindrical)

Geometry & Gap dis.(cm)	Power (Watts)	% CH ₄ Conv.	Reacted CH ₄ (moles/min)	Freq. (Hz)	Volt. (kV)	eV/(molecule of conv. CH ₄)
.27 (c)	118	24	.0015	100	7.6	49
.25 (p)	100	25	.0015	100	5.0	41

Table 3: 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.	% Ethane Select.	% CO Select	% CO ₂ Select	% Me Select.	% MF Select.	% FA Select.	% F Select.	% Et Select.	%Org. Liquid Sum	%Gas Phase Sum
6	23	67	3	11	10	11	3	15	15	1	45	24
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

Table 4: Cylindrical Reactor, 3:1 CH₄:O₂, 7.6 kV, 100 Hz, 200 cc/min

H ₂ O Temp.(° C)	Power (Watts)	Mole % CH ₄ Conv.	eV/(molecule of conv. CH ₄)
6	112	23	48
28	118	24	49
54	119	24	49
75	135	25	53

Table 5: Cylindrical Reactor, H₂:CO₂, 5.9 kV, 87 Hz, total flow rate =106 cc/min, H₂O jacket temp. =15°C

H ₂ :CO ₂ Ratio	% CO ₂ Conv.	% H ₂ Conv.	% CO Select.	Power (Watts)	eV/(molecule of conv. CO ₂)
3:1	10	3.9	117	96	570
4:1	11	3.5	104	100	614
5:1	13	3.3	94	102	640
6:1	13	2.6	101	103	788

Table 6: Cylindrical Reactor CO:H₂O, 7.0 kV, 90 Hz, total flow rate =106 cc/min, H₂O jacket temp. =80°C

% CO Conv.	% CO ₂ Select.	% H ₂ O Conv.	Power (watts)	eV/(molecule of conv. CO)
3.5	58	11	38	154

Table 7: CO₂:CH₄ experiments(5.5 kV, 80 % helium concentration, space time = 4 min.)

CO ₂ :CH ₄ Ratio	% CH ₄ Conv.	% CO ₂ Conv.	% Ethane Select.	% CO Select.	% Hydrogen Select.
1:2	22	16	65	34	9
1:1	16	9	23	76	2
2:1	28	13	65	34	14

Table 8: CO₂:CH₄ experiments(6.6 kV, 80 % helium concentration, space time = 4 min.)

CO ₂ :CH ₄	% CH ₄ Conv.	% CO ₂ Conv.	% Ethane Select.	% CO Select.	% Hydrogen Select.
1:2	25	16	67	32	10
1:1	24	14	13	87	1
2:1	34	15	34	66	16

Table 9: CO₂:CH₄ experiments(7.7 kV, 80 % helium concentration, space time = 4 min.)

CO ₂ :CH ₄	% CH ₄ Conv.	% CO ₂ Conv.	% Ethane Select.	% CO Select.	% Hydrogen Select.
0:1	15	-----	99	-----	4
1:2	29	21	65	34	12
1:1	30	18	17	82	7
2:1	40	18	31	68	20

Table 10: Effect of helium concentration on methane conversion(CO₂:CH₄ ratio 1:1, 5.5 kV, 4 min. space time)

Helium Conc.	% CH ₄ Conv.	% CO ₂ Conv.	% Ethane Select.	% CO Select.	% Hydrogen Select.
20 %	<1	<1	89	0	0
50 %	6	4	69	30	2
80 %	16	9	23	76	2

CONCLUSIONS

The results of this study show that product selectivities are strongly influenced by *in-situ* product condensation in partial oxidation of methane in a silent electric discharge reactor when reactor wall temperature is varied. At 28°C, 52 percent of the reacted carbon is recovered as these liquid organic oxygenates. At 75°C only 24 percent of the reacted carbon is recovered as "liquid" organic products. When the temperature of the system is lowered sufficiently the vapor pressures of the liquid organic oxygenates are reduced and condensation can occur, thus limiting the partial pressures of these desirable products in the gas phase. This results in reduced oxidation of these products to CO_x.

Experiments with hydrogen and carbon dioxide and with carbon monoxide and water suggest that the water-gas shift reaction pathway takes place in these systems. These results explain previous observations¹, where CO₂ inhibition and increased CO production were observed with higher CO₂ partial pressures, by demonstrating that the reverse water-gas shift reaction occurs.

Carbon dioxide reforming of methane in these systems also occurs along with methane coupling. The production of CO from methane under these conditions has not been established and methane partial oxidation from CO₂ is very limited. Finally, it appears that helium acts as a third body in enhancing methane conversion and affecting product selectivities. Its exact role in these reaction systems needs to be further studied.

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