Oxygen Pathways and Carbon Dioxide Utilization in Methane Partial Oxidation in Ambient Temperature Electric Discharges

D. W. Larkin, T. A. Caldwell, L. L. Lobban, and Richard G. Mallinson*

Institute for Gas Utilization Technologies, School of Chemical Engineering and Material Science, University of Oklahoma, 100 E. Boyd, Rm T 335, Norman, Oklahoma 73019

Received November 26, 1997. Revised Manuscript Received April 22, 1998

This methane conversion work studies a plasma reaction system for the production of organic oxygenates. The reactor consists of a glass dielectric interposed between the metal electrodes and a flowing gas stream through which kilovolt ac power with frequencies in the range of 100−200 Hz is applied. The geometry for this amounts to an annular system in which gas flows axially between the electrodes, with one electrode covered by a glass plate. The effect of the glass dielectric is to distribute the microdischarges across the entire electrode area and limit the duration of each microdischarge. The partial oxidation studies in this configuration produce methanol and other oxygenates (formaldehyde, formic acid, methyl formate). Selectivities for these products combined amount to 50−65%. These are the primary products when oxygen is included in the feed to the reactor. Thus far, experiments with low methane conversions have been conducted (up to around 25%) to minimize liquid condensation in the reactor. Byproducts here include significant levels of CO and CO_2, but it has been determined that CO_2 in the feed inhibits further production of CO_2 thereby eliminating net CO_2 production while increasing CO selectivity. These results show that oxygen appears to be needed in order to obtain higher methane conversions and significant oxygenated liquid organic products. CO or CO_2 does not appear to be a substitute for oxygen when trying to generate these desired oxygenated products.

Introduction

The relatively abundant resource of natural gas and its low cost and lower environmental impacts make this the carbon-based fuel of choice well into the twenty-first century. Additionally these same factors make it a desirable feedstock for production of a number of commodity chemicals.[1] There is additional need for new technologies which can also allow recovery of the many remote gas resources which are presently burned with no economic value and with significant negative environmental impact. Present technology uses steam reforming to produce synthesis gas which is converted to methanol and other chemicals. Substantial research is being conducted on more efficient direct routes to oxygenates through direct partial oxidation chemistry. None of the direct partial oxidation routes has achieved the breakthroughs needed in order to be competitive, although new methods using nonequilibrium plasmas and plasma-promoted catalysis appear to offer significant potential.[2−5] Additional research into enhancement of the carbon balance of methane conversion by reforming with CO_2 in order to "recycle" existing fully oxidized carbon is also being conducted. A significant additional motivation for this is the fact that much of the methane resource base occurs with significant CO_2 (natural gas, landfill gas, etc.) which must be removed at considerable expense before the methane is usable. Conversion processes which reduce or eliminate this requirement offer a significant economic advantage as well as environmental benefit.

Plasma reactors may provide a useful technology for this problem. These types of reactors are already being used to study possible applications in the control of NO_x, SO_x, CO_x, toxic gases, volatile organic compounds, hazardous emissions, and for ozone synthesis.[6] The plasmas can be equilibrium or nonequilibrium plasmas. Equilibrium plasmas can be created by arcing and achieve high gas temperatures. Nonequilibrium, low-temperature plasmas can be created through corona, glow, and silent discharge. Microwaves can also create plasmas and can fall under either category depending on the conditions.[7]

This study uses a silent electric discharge to cause the reaction of methane to form oxygenated products. This discharge is created with an ozone type barrier discharge reactor connected to an ac power source. A nonspark high-energy environment is created that allows low gas temperatures to exist in a high electron

---

(1) Fox, J. M., III *Catal. Rev.-Sci. Eng.* **1993**, *35* (2), 169−212.

(2) Liu, C. A.; Marafee, A.; Hill, B.; Xu, G.; Mallinson, R. G.; Lobban, L. L. *Ind. Eng. Chem. Res.* **1996**, *35*, 3295.

(3) Bhatnagar, R.; Mallinson, R. G. *Methane and Alkane Conversion Chemistry*; Plenum Press: New York, 1995; p 249.

(4) Marafee, A.; Liu, C. A.; Xu, G.; Mallinson, R. G.; Lobban, L. L. *Ind. Eng. Chem. Res.* **1997**, *36*, 632.

(5) Liu, C. A.; Marafee, A.; Hill, B.; Mallinson, R. G.; Lobban, L. L. Methane Conversion to Higher Hydrocarbons over Charged Metal Oxide Catalysts. *Appl. Catal. A.*, in press .

(6) Chang, J. S.; Lawless, P. A.; Yamamoto, T. *IEEE Trans. Plasma Sci.* **1991**, *19*, no. 6.

(7) Dr. Changjun Liu, personal communication, December 1997.

S0887-0624(97)00217-X CCC: $15.00

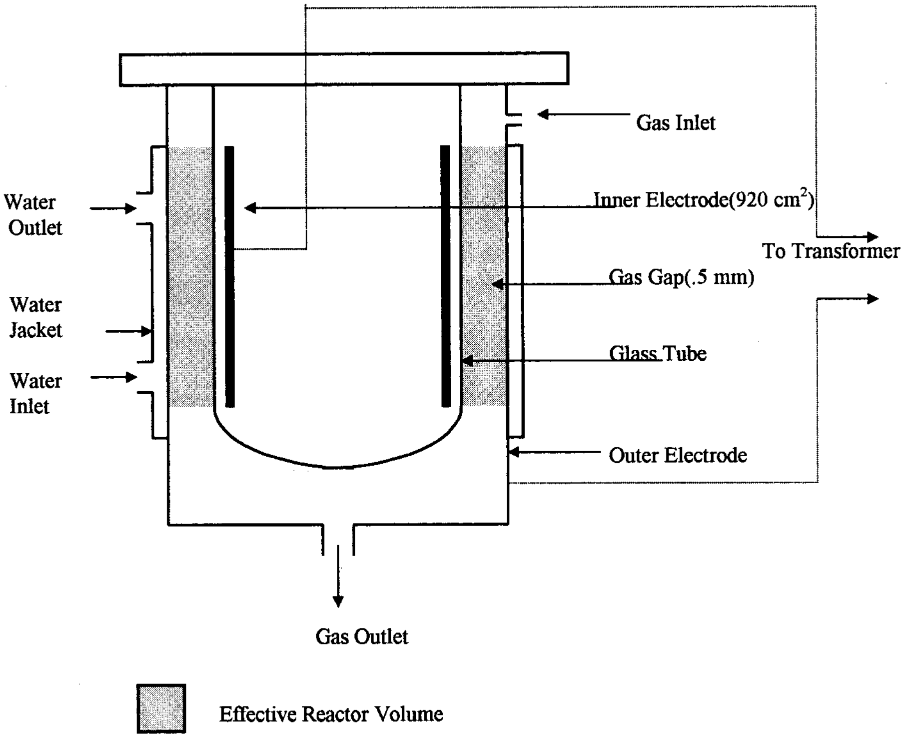

Figure 1. Plasma reactor diagram (annular volume = 225 mL).

temperature environment.[6] The purpose of this study is to determine the effect of CO_2 and CO on the partial oxidation of methane in a nonequilibrium plasma environment as well as to study the oxygen pathways involved in this system. This research is an extension of Bhatnagar and Mallinson's work.[3] Due to enhanced analysis capabilities there is improvement in the speciation of the oxygenated liquid products. The general trends from the previous study still hold to be true; however, through GC−MS analysis the significant liquid oxygenate products are found to be methanol, methyl formate, formaldehyde, and formic acid, and ethanol is produced only in small amounts.

Experimental Section

To conduct the partial oxidation experiments a plasma reactor is used. Gas cylinders are used to store and supply the gas to the reactors. Mass flow controllers, made by Porter Instrument Company, regulate the flow rates of these gases. Once the gases flow through the mass flow controllers, the streams are combined. The feed gas enters the annular plasma reactor at the top. The reactor consists of two concentric cylinders with glass on the outer wall of the inner cylinder and are separated from each other 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 "microdischarge" streams which are uniformly dispersed throughout the volume between the electrodes. From exterior to interior, as seen in Figure 1, the reactor layers are comprised of a water jacket, outer stainless steel electrode, gas gap, glass plate, and inner stainless steel electrode. The products then exit the reactor from the bottom. The gap the gas flows through is 0.5 mm wide. The active reaction area is 920 cm^2. The effective annular volume of the reactor is then 225 mL.

The ac power supply to the reactor is an Elgar model 501SL. A CBK Precision function generator is used in conjunction with the power supply to form a sinusoidal waveform which is supplied to the reactor. This output voltage is stepped up by 125 times through the use of a transformer and is supplied to the reactor. Once through the reactor, the product stream is fed through a trap cooled by dry ice and acetone which is at −40 °C. Methanol, methyl formate, formic acid, formaldehyde, and water are condensed out. The remaining gas 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 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.

Four types of experiments are conducted in this study. The first two involve using a stream of methane, oxygen, and carbon monoxide or methane, oxygen, and carbon dioxide. The CO_x flow rate is varied between 0 and 60 cm^3/min. All of these experiments have a 200 cm^3/min total flow rate. The methane-to-oxygen ratio is kept constant at 3:1. The frequency and voltage are set at 100 Hz and 8.5 kV. The third type of experiment feeds methane, oxygen, carbon monoxide, and carbon dioxide to the plasma reactor. The methane-to-oxygen ratio ranges from 2.65:1 to 3:1. The frequency and voltage are kept at 100 Hz and 8.5 kV for these experiments. The last type of experiment involves feeding pure methane or streams of methane with carbon dioxide, or with carbon monoxide, or with helium, or with carbon dioxide and carbon monoxide to the reactor. The frequency and voltage for all of these experiments are 200 Hz and 16 kV.

For all of the experiments, the carbon selectivity is defined as the total number of moles of carbon formed of a particular product divided by the total number of moles of carbon reacted (calculated from molar flow rates). If the only carbon source is methane, the calculation is straightforward. Moles of methane fed to the reactor minus the moles of methane leaving the reactor gives the total number of moles of carbon that have reacted. The calculation becomes a little more complicated if carbon monoxide or carbon dioxide are added to the feed stream. If there is a net loss in carbon monoxide or carbon dioxide, then the moles of carbon that have reacted from these compounds are added to the moles of carbon from the methane

Table 1. Frequency/Voltage Experimental Results[a]

freq (Hz)	voltage (kV)	mol % CH_4 conv	mol % O_2 conv	% CO select.	% CO_2 select.	% methanol select.	% methylformate select.	% formic acid select.	% formaldehyde select.	org liq sum	% ethane select.
100	8.5	20.2	67.0	15.3	12.2	15.0	10.3	15.8	11.5	52.6	3.7
200	16.0	14.0	48.0	18.2	15.3	13.3	8.8	16.0	11.9	50.0	4.7

[a] 200 mL/min flow rate and 3:1 CH_4:O_2.

Table 2. CO Experimental Results[a]

CO flow rate (mL/min)	mol % CH_4 conv	mol % CO conv	mol % O_2 conv	% CO select.	% CO_2 select.	% methanol select.	% methylformate select.	% formic acid select.	% formaldehyde select.	org liq sum	% ethane select.
0	20.2	0.0	67.0	15.3	12.2	15.0	10.3	15.8	11.5	52.6	3.7
10	17.0	0.0	63.1	6.6	20.5	17.3	14.7	12.9	12.0	56.9	4.9
20	18.6	4.7	65.7	0.0	23.8	17.0	12.2	13.5	11.6	54.3	5.2
40	19.8	8.1	78.1	0.0	31.2	15.5	11.5	12.5	9.6	49.1	6.9
60	17.9	7.4	74.0	0.0	36.9	12.1	12.4	3.7	5.8	34.0	8.0

[a] 3:1 CH_4:O_2, 8.5 kV, 100 Hz, 200 mL/min flow rate.

Table 3. CO_2 Experimental Results[a]

CO_2 flow rate (mL/min)	mol % CH_4 conv	mol % CO_2 conv	mol % O_2 conv	% CO select.	% CO_2 select.	% methanol select.	% methylformate select.	% formic acid select.	% formaldehyde select.	org liq sum	% ethane select.
0	20.2		67.0	15.3	12.2	15.0	10.3	15.8	11.5	52.6	3.7
10	14.9		53.4	22.8	13.6	14.3	9.4	10.0	11.8	45.5	4.5
20	21.9		69.7	21.3	1.6	19.0	17.5	8.2	6.7	51.4	3.0
40	25.9	4.0	77.2	29.4	0.0	11.9	20.8	21.2	12.5	66.4	2.7
60	22.2	3.3	70.6	42.2	0.0	11.1	7.6	7.3	8.4	34.4	3.5

[a] 3:1 CH_4:O_2, 8.5 kV, 100 Hz, 200 mL/min flow rate.

reacted, giving the total moles of carbon reacted. The conversion is simply defined as the difference between moles of a feed component in and moles of that feed component out divided by moles of the feed component in. Thus, any feed component which has a net loss in moles during the reaction will have its conversion calculated.

Results and Discussion

The base experiment for this study is with methane and oxygen only. This follows the work Mallinson et al. (1987) and Bhatnagen and Mallinson (1995). In this study the product analysis, as already mentioned, has been refined and use has been made of the variables studied in the previous work in order to determine optimum conditions for liquids production. This work has been conducted under conditions which limit the conversion to 20−25% due to the condensation of liquid products in the reactor which interfere with the discharge behavior in the gap.

Frequency has been found to be a significant variable affecting the performance of the reactor system. Table 1 compares the results at 100 and 200 Hz for the methane oxygen system. The two significant differences in these experiments are the methane and oxygen conversions. At 200 Hz the conversion for methane is 14% while conversion for oxygen is 48%. When frequency is decreased to 100 Hz the methane and oxygen conversion increase to 20.2% and 67.0%, respectively. The product selectivities, on the other hand, do not significantly change. A more detailed study has been made using a pure hydrocarbon reactant by Caldwell et al. (1997).

The next set of experiments varies the flow rate of CO in a 3 to 1 methane and oxygen stream. The results can be seen in Table 2. As the CO flow rate increases, the net selectivity for CO decreases from 15.3% to 0% while the selectivity for CO_2 increases from 12.2% to 36.9%. With a flow rate of 20 cm^3/min or greater of CO, the rate of its destruction is greater than the rate of its creation and, thus, produces a net selectivity of zero. When comparing the results with the results of the experiment which had no CO in the feed, it is apparent that the liquid product selectivities are unaltered. The one exception to this is when the CO feed flow rate is 60 cm^3/min. At this point the liquid product selectivities decrease. This occurs because as the CO flow rate is increased the oxygen feed flow rate decreases. As oxygen becomes sufficiently limited, the production of the oxygenated liquid products decreases. These results show that the contribution from CO to the formation of liquid products is evidently negligible and that CO is not an intermediate product leading to liquids production but on the contrary appears to be a precursor to CO_2. Another result of the increase in CO is the increase in the selectivity for ethane. Without CO, ethane's selectivity is 3.7%, while at a 60 cm^3/min CO flow rate its selectivity increases to 8%. Thus, the effect on the activation of methane is less than on oxygenate production as methane conversion drops only a few percent from its original value. The limited oxygen environment increases the probability of coupling of activated methane.

The next set of experiments is run with CO_2 present instead of CO in the feed stream. The CO_2 experimental results can be seen in Table 3. In these experiments, as the CO_2 feed flow rate increases, the CO_2 selectivities decrease while the CO selectivities increase. The liquid selectivities, as is the case in the CO experiments, are unaffected when CO_2 is fed into the feed stream until the CO_2 flow rate is raised to 60 cm^3/min. At this flow rate, the liquid oxygenates selectivities start to decrease because of the reduced oxygen concentration. The net

Table 4. CO_2/CO Experimental Results[a]

expt[b]	mol % CH_4 conv	mol % O_2 conv	% CO select.	% CO_2 select.	% ethane select.	% methanol select.	% methyl-formate select.	% formic acid select.	% form-aldehyde select.	org liq sum
1	20.2	78.8	7.2	15.3	4.9	16.5	11.6	15.2	11.8	55.1
2	18.9	77.3	14.6	14.7	4.8	20.2	12.9	17.6	13.6	64.3

[a] 8.5 kV, 100 Hz. [b] Experiment 1: $CH_4 = 125$ mL/min, $O_2 = 41$ mL/min, $CO_2 = 17$ mL/min, CO = 17 mL/min. Experiment 2: $CH_4 = 130$ mL/min, $O_2 = 49$ mL/min, $CO_2 = 17$ mL/min, CO = 10 mL/min.

Table 5. No O_2 Experimental Results

CH_4 flow rate (mL/min)	He, CO_2, and/or CO flow rate (mL/min)	mol % CH_4 conv	mol % CO conv	mol % CO_2 conv	% CO select.	% CO_2 select.	% ethane select.
200	0	3.3	0.0	0.0	0.0	0.0	48.7
150	50 He	3.5	0.0	0.0	0.0	0.0	56.6
150	50 CO_2	3.4	0.0	1.2	44.6	0.0	37.4
150	50 CO	3.4	0.1	0.0	0.0	1.3	82.2
150	40 CO/ 40 CO_2	7.0	2.3	3.2	0.0	0.0	47.6

CO_2 selectivity becomes zero when the CO_2 feed flow rate is 40 cm^3/min or greater. This, again, is because the rate of destruction of CO_2 is greater than the rate of creation at this partial pressure of CO_2. These results suggest that CO_2, like CO, does not enhance liquid production. Of great interest, however, is the fact that CO_2 is evidently converted to CO, without the loss of liquids production except under oxygen-limited conditions. The decrease in methane conversion observed in these experiments is also relatively small. Thus, the presence of CO_2 does not materially interfere with methane conversion or oxygenated production and is to some extent converted to a more useful product. Due to recent enhanced analysis capabilities it has been shown that hydrogen is being produced in significant amounts.

The third set of experiments examined addition of both CO and CO_2 to the methane and oxygen feed stream. These results can be seen in Table 4. The total flow rate, frequency, and voltage are the same as the previous experiments. When both CO and CO_2 flow rates are both set at 17 cm^3/min, net CO_2 selectivity is 15% while net CO selectivity is 7%. This suggests the rate for CO conversion to CO_2 is greater than the rate of CO_2 conversion to CO at these partial pressures and 1 min residence time. The second experiment reduces the CO flow rate to 10 cm^3/min while keeping the CO_2 flow rate at 17 cm^3/min. This causes both selectivities to be around 15%. This is due to the fact that with more CO_2 in the feed stream more CO is produced, as was also seen in the CO_2 experiments, and the rates are in balance.

The last set of experiments, shown in Table 5, are with a pure CH_4 feed or gas mixtures of 150 cm^3/min of methane with 50 cm^3/min of helium, or CO_2, or CO, or 40 cm^3/min of CO and CO_2. The first three experiments in Table 5 give ethane selectivities which range from 37% to 57%. Little or no liquid products or solid accumulation in the reactor was observed. The rest of the products are assumed to be C_3+ compounds, but analysis of these was not available. When methane is the only feed gas, ethane selectivity is 49%. It is interesting to note that the mixture of CH_4 and CO_2 produced a total selectivity for liquid products of less than 5%. When methane is fed with CO, less than 2% of the total selectivity is for liquids. This again indicates that the contribution from CO or CO_2 to liquid products formation is negligible. The selectivity for ethane is 82% when methane and CO are fed. This suggests, as is shown in the CO experiments, that CO in the feed stream appears to promote methane coupling. It seems to be a better promoter than CO_2 since with CO_2 an ethane selectivity of only 37% is obtained. Note in all these cases the absence of oxygen dramatically reduces the conversion of methane. The successful activation of methane to cause its conversion significantly depends on active species generated by O_2 which are not formed from CO or CO_2.

Pathways that could be occurring in the homogeneous partial oxidation of methane have been studied.[8,9] A study involving O_2 and O_3 in the feed with CH_4 show that at 401 °C no methanol could be detected with just O_2 and CH_4 but methanol was detected when O_3 was present at the same temperature. The authors suggested that O_3 decomposed to O_2 and O and the O atom could abstract hydrogen from methane to form CH_3 and OH. Once the methyl radical is generated, a series of reactions can occur which ultimately lead to the products.[8] At ambient temperature, Mallinson found no reaction between methane and O_3/O_2 mixtures.[10] Also, the possible reaction of activation of CO_2 via dissociation

$$CO_2 + e^- \rightarrow CO + O + e^-$$

or by electron attachment

$$CO_2 + e^- \rightarrow CO + O^-$$

does not appear to generate the required energetic species for significant methane activation.

Conclusions

Methane and oxygen mixtures may be converted to a significant extent to liquid products: methanol, formaldehyde, formic acid, and methyl formate in a low-temperature, atmospheric pressure, plasma environment. CO, CO_2, H_2, and ethane are also products. Ethane becomes the primary product in an oxygen-limited environment. High conversions of methane and of significant liquid oxygenates require O_2 to be present. It is believed that the oxygen species generated in the plasma field somehow activates the methane in such a manner that allows for these higher conversions. At this point the pathways appear to generate CO from

---

(8) Gesser, H. D.; Hunter, N. R.; Das, P. A. The Ozone Sensitized Oxidation Conversion of Methane to Methanol and Ethane to Ethanol. *Catal. Lett.* **1992**, *16*, 217−221.

(9) Rotzoll, G. Mass Spectrometric Investigation and Computer Modeling of the CH_4−O_2−O_3 Reaction from 480 to 830 K. *J. Phys. Chem.* **1986**, *90*, 677.

(10) Mallinson, R. B. Unpublished results, 1987.

stepwise oxidation from methane which is then oxidized to CO_2 via the water gas shift reaction. Recent hydrogen detection enhancements to the gas chromatograph have shown that hydrogen is being produced when methane is combined with oxygen which, therefore, allows the water gas shift reaction to take place. A pseudo-equilibrium is established which can be driven toward the shift or toward the reverse shift depending on the composition. Reduction of CO to more useful products does not occur to a significant degree under the present conditions, although CO_2 hydrogenation is known to be possible.[11] The presence of CO_2 inhibits further production of CO_2 from overoxidation and contributes to “recycling” of carbon.

Acknowledgment. The United States Department of Energy under Contract DE-FG21-94MC31170 and the National Science Foundation for a Graduate Research Traineeship are gratefully acknowledged.

EF970217N

---

(11) Eliason, B.; Kogelschatz, U.; Xue, B.; Zhou, L. M. Application of Dielectric-Barrier Discharges To The Decomposition And Utilisation of Greenhouse Gases. 13th International Synposium on Plasma Chemistry (ISPC-13), Beijing, Aug 1997.