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รายงานวิจัยฉบับสมบูรณ์

โครงการ

ปฏิกิริยาร่วมการเปลี่ยนรูปของคาร์บอนไดออกไซด์และไอน้ำกับมีเทนในพลาสมาอุณหภูมิต่ำ

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สิงหาคม 2545

สัญญาเลขที่ BGJ/10/2543

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ABSTRACT

Project Code : BGJ43-8-0010

Project Title : Combined Carbon Dioxide and Steam Reforming with Methane in Low Temperature Plasmas

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The combination of carbon dioxide reforming and steam reforming with methane was investigated in a corona discharge reactor with moderate power consumption. The plasma was used to overcome the energy barrier of these two endothermic reactions instead of high temperature catalytic processes. Simultaneous carbon dioxide and steam reforming produced higher methane conversions and CO/C_2 ratios than only steam reforming or carbon dioxide reforming. The H_2/CO ratio of 1.9:1 is close to that desired for Fischer Tropsch or methanol synthesis was achieved at a CO_2/CH_4 ratio of 1:1 with 50% water-vapor in the feed stream. In this condition, the energy consumption was about 12 eV/molecule of carbon converted. Using electricity to drive the reaction at low temperature is counter-balanced by lower costs and simpler operation.

บทคัดย่อ

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ชื่อโครงการ : ปฏิกิริยาร่วมการเปลี่ยนรูปของคาร์บอนไดออกไซด์และไอน้ำกับมีเทนในพลาสมาอุณหภูมิต่ำ

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คำหลัก : การเปลี่ยนรูปของคาร์บอนไดออกไซด์, การเปลี่ยนรูปของไอน้ำ, กระแสไฟฟ้าโคโรนา

การทดลองนี้เป็นการศึกษาปฏิกิริยาร่วมการเปลี่ยนรูปของคาร์บอนไดออกไซด์และการเปลี่ยนรูปของไอน้ำกับมีเทนในเตาปฏิกรณ์แบบโคโรนาซึ่งต้องการพลังงานปานกลาง พลาสมาสามารถข้ามระดับพลังงานในการเกิดปฏิกิริยาดูดความร้อนทั้งสองปฏิกิริยานี้ได้แทนการใช้กระบวนการเร่งปฏิริยาที่อุณหภูมิสูง การรวมปฏิกิริยาการเปลี่ยนรูปของคาร์บอนไดออกไซด์กับมีเทนและปฏิกิริยาการเปลี่ยนรูปของไอน้ำกับมีเทนสามารถทำให้การเปลี่ยนมีเทนและอัตราส่วนของคาร์บอนมอนอกไซด์ต่อไฮโดรคาร์บอนที่มีคาร์บอน 2 อะตอมสูงกว่าปฏิกิริยาเปลี่ยนรูปไอน้ำหรือปฏิกิริยาเปลี่ยนรูปคาร์บอนไดออกไซด์อย่างใดอย่างหนึ่ง ก๊าซขาเข้าที่มีอัตราส่วนของคาร์บอนไดออกไซด์ต่อมีเทน 1:1 และไอน้ำ 50 เปอร์เซ็นต์สามารถผลิตผลิตภัณฑ์ที่มีอัตราส่วนของไฮโดรเจนต่อคาร์บอนมอนอไซด์ที่ 1.9:1 ซึ่งเป็นอัตราส่วนที่เหมาะสมในการสังเคราะห์ฟิชเชอร์โทรปหรือการสังเคราะห์เมทานอล ในสภาวะที่ใช้นี้พลังงานที่ถูกใช้มีค่าประมาณ 12 อิเล็กตรอนโวลต์ต่อโมเลกุลของคาร์บอนที่ถูกเปลี่ยนไป การใช้กระแสไฟฟ้าเป็นแรงขับดันให้เกิดปฏิกิริยาที่อุณหภูมิต่ำเป็นการลดค่าใช้จ่ายและสามารถดำเนินการได้ง่ายขึ้น

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CHAPTER I

INTRODUCTION

With increasing population and rapid technology development, we have been facing alteration of the climate. Greenhouse gases that include carbon dioxide, methane, ozone, halocarbons and nitrous oxide, to significant extents come from the combustion of fossil fuels (coal, oil, and natural gas) for power generation and transportation. A potentially useful reaction for reducing the impact of carbon dioxide (reducing net emissions), a major component in many natural gas resources, especially in Asia, is carbon dioxide reforming with methane (Reaction 1) for production of synthesis gas (carbon monoxide and hydrogen) at a lower H_2/CO ratio compared to steam reforming of methane (Reaction 2), which is a major conventional process for synthesis gas production. A typical industrial steam reformer operates at 1,120-1,170 K and 15-30 atm over a Ni/Al_2O_3 catalyst (1). However, as with steam reforming, the highly endothermic reaction requires significant high temperature energy input that is usually provided by combustion that releases carbon dioxide. Also, the 1:1 H_2/CO ratio produced from carbon dioxide reforming requires, for GTL applications, the use of the water gas shift reaction, in which much of the potential net consumption of carbon dioxide is lost. However, a major problem with carbon dioxide reforming to this point in time is the deactivation of the catalyst due to carbon deposition (Reactions 3 and 4) at the desired reaction conditions.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ mol}^{-1} \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206 \text{ kJ mol}^{-1} \qquad (2)$$

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 75 \text{ kJ mol}^{-1} \qquad (3)$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H = -172 \text{ kJ mol}^{-1} \qquad (4)$$

So far, There is no any effective commercial catalyst which can operate without carbon formation (2). One of possible alternatives is to combine carbon dioxide reforming with steam reforming. A thermodynamics study has shown that the presence of water in carbon dioxide reforming allows increased methane conversion (3) and probably decreased carbon formation at a specific CO_2/CH_4 ratio. Moreover, for several feed ratios of CH_4/CO_2, the desired H_2/CO ratio at equilibrium is controllable by the amount of water added in feed stream, for example, the desired ratio of H_2/CO of 1:1 can be obtained from a Terrell natural gas by using up to 3.28% of water in the feed (3). Both carbon dioxide reforming and steam reforming have similar low net carbon dioxide reduction due to combustion needed to provide the required heat of reaction. Thus any net reduction of carbon dioxide impact from the process must be compared with partial oxidation or combined/autothermal reforming which is exothermic or self heating, but require the production of oxygen that is itself energy intensive. Therefore, rather than considering the net carbon dioxide reduction as the driver, other factors must be considered. For example, high carbon dioxide in natural gas resources may be stranded by the high cost of carbon dioxide removal, which may be reduced or eliminated by use of carbon dioxide reforming. Additionally, the possible lower capital investment and operating costs due to the elimination of the requirement for oxygen makes consideration of this technology worthwhile. Due to the fact that both carbon dioxide reforming and steam reforming are endothermic reactions, the high reaction temperature requires an intensive energy input and a high operating cost. One may uses non-equilibrium plasma to reduce energy cost instead of thermal process.

The non-thermal, also called cold plasma, with its non-equilibrium properties, high electron temperature and low bulk gas temperature, provides the capability for initiating chemical reactions at low temperatures and potentially with low energy input. The non-equilibrium plasma is used to overcome the energy barrier to start the reaction by promoting radical production (4).

Corona discharge and dielectric barrier discharge (DBD) techniques are two of the commonly used methods for producing non-equilibrium plasmas at atmospheric pressure (5). The utilization of the non-equilibrium plasma techniques for carbon dioxide reforming with methane has been studied in the dielectric barrier discharge (2, 6-8).

The spectroscopic characteristic of a plasma created in a methane and carbon dioxide mixture by a high-voltage, steep front-voltage, very-short-pulse triggered dielectric barrier discharge in a tubular cell was investigated. The very steep front voltage ($>10^{12}$ V/s) allowed the reactor to operate at higher reduced field values (E/n) than in conventional DBD systems. To confirm the properties of the non-equilibrium plasma, it was shown that the temperature inside the streamers was around 3,000 K and the mean gas temperature in the active volume was close to room temperature (6).

The effects of CO_2/CH_4 ratio and adding helium to a 1:1 CO_2/CH_4 ratio feed stream were studied. The results indicated that CO_2/CH_4 ratio strongly affected the results. Increasing the partial pressure of carbon dioxide from a 1:2 to 1:1 CO_2/CH_4 ratio caused increased carbon dioxide conversion to carbon monoxide but reduced the ethane and hydrogen selectivities. A further increase in the CO_2/CH_4 ratio from 1:1 to 2:1 caused an increase in ethane and hydrogen selectivities. Despite lowering methane partial pressure, helium acts as a third body in enhancing methane conversion and carbon monoxide selectivities (7).

A numerical simulation was performed to investigate the conversion of methane and carbon dioxide to synthesis gas in a DBD reactor. Using curve-fitting, the H_2/CO ratio can be presented as a simple function of a mixing ratio of CH_4/CO_2 which can be approximated over a wide range. Specific electric energy, gas pressure, and temperature hardly influence syngas composition (2).

The combination of solid catalysts with a dielectric-barrier discharge also has been studied for carbon dioxide reforming of methane. It was shown that the nickel and the nickel-calcium coated foams showed nearly identical activities for the reforming reaction in the discharge in the temperature range of 40 - 230 °C and gave significantly higher carbon monoxide production than the rhodium coated catalyst and the uncoated foam. The reaction was operated over the stoichiometric ratio at a CO_2/CH_4 ratio of 3:1 to minimize hydrocarbon formation. After the reaction, small amount of carbon or carbonaceous deposits were found on the foams (8).

Because the corona discharge is particularly easy to establish, it has had wide application in a variety of processes such as electrostatic precipitation, electro-photography, static control in semiconductor manufacture, ionization instrumentation, destruction of toxic compounds, generation of ozone, and synthesis of chemicals (9).

In this work, a corona discharge reactor was used to facilitate carbon dioxide reforming by itself and in combination with steam at low temperatures. This has been shown to be possible in other methane conversion studies without carbon dioxide, such as helping in the conversion of methane over Sr/La_2O_3 (10) and other materials (11). The disadvantage of using electrical energy, that at best may only be about 60 percent efficient, may be offset by process simplicity and cost, lower carbon formation and less excess energy that must be recovered and utilized only with considerable cost.

CHAPTER II

EXPERIMENTAL SECTION

The schematic diagram of the studied corona discharge system used throughout this study is illustrated in Figure 2.1. The flow rates of feed gases were controlled by a set of mass flow controllers supplied by Porter Instrument, Inc. Water-vapor was introduced into the reactor by passing the feed gases through a water-bath of which the temperature was controlled to adjust the concentration of water-vapor in the feed gas mixture. The feed gases were well mixed and then flowed downward through the reactor. The reactor temperature was controlled to be constant 100 °C to avoid water condensation during reaction. All the experiments were operated at atmospheric pressure. The feed gases and the exhaust gases from the reactor were introduced into two condensers in series cooled by ice water to remove the condensable products as well as water and then analyzed on-line by a Carle AGC 400 gas chromatograph with thermal conductivity detector. However, no organic products were collected from the condensers when analyzed with a Varian 3300 GC with a Porapak Q Column. The power supply unit consisted of an AC power supply for converting domestic AC power 120 V, 60 Hz, using a function generator to vary the frequency in the range of 300 to 600 Hz with a sinusoidal waveform. The output was then transmitted to a high voltage alternating current (HVAC) transformer. The HVAC transformer could step up the low side voltage to the high side voltage by a nominal factor of 125 at 60 Hz. This factor may not be constant with changes in frequency due to changes in the power factor because of the capacitive nature of the reactor system. The discharge occurred between two stainless steel electrodes in a quartz tube with an inside diameter of 7 mm. The gap distance between these two electrodes was 1 cm. The feed gas flow rate was the same for every experiment at 100 sccm corresponding to a residence time of 0.23 s. The upper wire electrode was centered axially within the reactor tube, while the lower electrode was a circular plate with holes to allow gas to pass through the reactor and positioned perpendicular to the reactor axis. An Extech power analyzer was used to measure the power, power factor, current, frequency, and voltage at the low side of the power circuit.

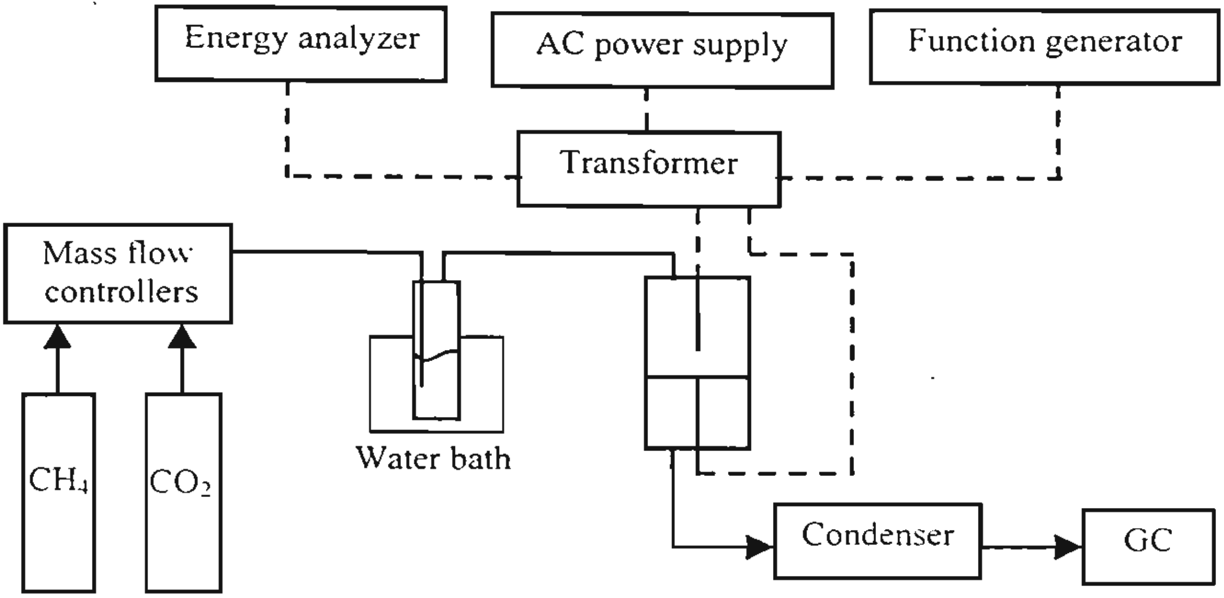

Figure 2.1 Schematic diagram of corona discharge reactor.

For this system, the energy consumption for conversion of carbon in the feed gas consisting of methane and carbon dioxide is given in units of electron-volt/molecule of carbon converted (eV/m_C). S_X is defined as the selectivity based on converted carbon in both carbon dioxide and methane. S_{total} is defined as the total selectivities of all products which contain C (carbon atom).

All experiments had a carbon balance greater than 84%. Water was not quantified.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Reaction Pathways in Plasma Environment

The electron energy, which corresponds to the electron temperature, is restricted to less than 6 eV in the corona discharge (12). These relatively low-energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than 12 eV (13), but high enough to dissociate carbon dioxide molecules with dissociation energies of 5.5 eV (Reaction 5) (2, 5, 14).

$$e^- + CO_2 \rightarrow CO + O + e^- \qquad (5)$$

H_2O also requires only a relatively low electron energy to be dissociated to produce O, H and OH radicals as shown in Reactions 6 and 7 (15):

$$e^- + H_2O \rightarrow O^- + H_2 \qquad (6)$$

$$e^- + H_2O \rightarrow OH^- + H \qquad (7)$$

These radicals, H, OH and O, further abstract hydrogen from methane to form methyl radical (CH_3) leading to a significant rate of methane conversion in the corona discharge (Reactions 8-10).

Methyl radical formation :

$$CH_4 + O \rightarrow CH_3 + OH \qquad (8)$$

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad (9)$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (10)$$

These methyl radicals react further to either combine with another CH_3 to form ethane (Reaction 11) or break down into CH_2, CH and C and subsequently form ethylene, acetylene and carbon oxides (16). Ethane can be further dehydrogenated to form ethylene and acetylene and ethylene can be dehydrogenated to form acetylene.

These reaction pathways were also observed in the conversion of methane via microwave plasmas (17). The coupling of hydrogen radicals forms hydrogen. Beyond these main reactions, there maybe many contributing reaction pathways in the corona discharge environment. Some of the possible ethane, ethylene, acetylene and hydrogen formation reactions are shown in Reactions 11-39. Water may be formed in the discharge via Reactions 40-43.

Ethane formation :

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{11}$$

$$CH_4 + CH_2 \rightarrow C_2H_6 \tag{12}$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \tag{13}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 \tag{14}$$

Ethylene formation :

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{15}$$

$$C_2H_6 \rightarrow CH_3 + CH_3 \tag{16}$$

$$CH_3 + CH_3 \rightarrow C_2H_4 + H_2 \tag{17}$$

$$CH_3 + CH_2 \rightarrow C_2H_4 + H \tag{18}$$

$$CH_2 + CH_2 \rightarrow C_2H_4 \tag{19}$$

$$CH_3 + CH_3 \rightarrow C_2H_5 + H \tag{20}$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \tag{21}$$

$$C_2H_6 + CH_3 \rightarrow CH_4 + C_2H_5 \quad (22)$$

$$C_2H_5 + H \rightarrow CH_3 + CH_3 \quad (23)$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2 \quad (24)$$

Acetylene formation :

$$C_2H_4 \rightarrow C_2H_2 + H_2 \quad (25)$$

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \quad (26)$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 \quad (27)$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \quad (28)$$

$$CH + CH \rightarrow C_2H_2 \quad (29)$$

$$CH_2 + CH \rightarrow C_2H_2 + H \quad (30)$$

CO_x formation :

$$CH_3 + O \rightarrow HCHO + H \quad (31)$$

$$HCHO + O \rightarrow OH + CHO \quad (32)$$

$$CHO + O \rightarrow OH + CO \quad (33)$$

$$CHO + O \rightarrow CO_2 + H \quad (34)$$

$$HCHO + H \rightarrow H_2 + CHO \quad (35)$$

$$CHO + H \rightarrow H_2 + CO \quad (36)$$

$$HCHO + OH \rightarrow CHO + H_2O \quad (37)$$

$$CHO + OH \rightarrow CO + H_2O \quad (38)$$

Hydrogen formation :

$$2H \rightarrow H_2 \quad (39)$$

Water formation:

$$OH + H \rightarrow H_2O \quad (40)$$

$$OH + C_xH_y \rightarrow H_2O + C_xH_{y-1} \quad (41)$$

$$2H + O \rightarrow H_2O \quad (42)$$

$$H_2 + O \rightarrow H_2O \quad (43)$$

Moreover, the radicals of H, OH, and O generated from dissociation of water are essential ingredient for the inhibition and removal of carbon deposits which have a negative effect on gas discharges, shown in Reactions 44 and 45 (18).

$$C_{(s)} + H \rightarrow CH \quad (44)$$

$$CH_{(s)} + H \rightarrow CH_2 \quad (45)$$

3.2 Effect of Carbon Sources with Water-Vapor

In Table 2.1, the results of a feed stream of 50% methane or carbon dioxide or carbon monoxide reacting with 50% water are shown. Many products, CO, CO_2, C_2H_6,

C_2H_4, C_2H_2, and H_2, were produced from methane reacting with water but C_2 products were not produced from carbon dioxide with water or from carbon monoxide with water. Apart from the main reaction of methane reforming with steam in the corona discharge environment, there are also other reactions occurring simultaneously such as hydrogenation, dehydrogenation etc.

Table 2.1 Reactions of methane, carbon dioxide, carbon monoxide with water-vapor.

Carbon (%)	50% CH_4	50% CO_2	50% CO
Water-vapor (%)	50	50	50
Low side Voltage (V)	57	85	63
Frequency (Hz)	600	400	600
Power (W)	13	10	7
Power Factor	0.48	0.27	0.49
Current (A)	0.48	0.44	0.23
C conversion (%)	$X_{CH4} = 27$	$X_{CO2} = 1$	$X_{CO} = 6$
S_{CO} (%)	35	112	-
S_{CO2} (%)	1	0	105
S_{C2H6} (%)	5	0	0
S_{C2H4} (%)	8	0	0
S_{C2H2} (%)	39	0	0
S_{total} (%)	88	112	105
Energy consumption (eV/m_C)	14	353	35
H_2/CO_x	$H_2/CO = 4.7$	$H_2/CO = 0.0$	$H_2/CO_2 = 0.9$
CO/C_2	1.4	-	-
CO/O_2	-	2.3	-

The H_2/CO ratio is quite high; more than the stoichiometric ratio for steam reforming. In the industrial catalytic process, the syngas ratio (H_2/CO) obtained with steam reforming is higher than 3 caused by a surplus of steam (19, 20). High hydrogen production here results from the net dehydrogenation with the formation of C_2 hydrocarbon products and hydrogen also can be produced directly from the dissociation of water in the corona discharge as shown in Reaction 6. Steam reforming of methane in the low temperature plasma environment is an alternative way to produce synthesis gas instead of the conventional process.

Carbon dioxide with water is essentially unreactive under the conditions of this experiment, where of course both species are strongly favored by thermodynamics. Even though methane with water and carbon dioxide with water have the same current, or an equal the number of electrons to initiate reactions, carbon dioxide conversion is much lower than methane conversion. The products were only oxygen and carbon monoxide with a CO/O_2 ratio of 2.3. Carbon monoxide with water is converted to some extent with the expected production of hydrogen and carbon dioxide. For the CO/H_2O system, the H_2/CO_2 was about 0.9, that is close to the stoichiometric ratio of the water gas shift reaction. Energy consumption of carbon dioxide with water and carbon monoxide with water is very high under these conditions.

3.3 Effect of Water-Vapor on Carbon Dioxide Reforming with Methane

In Table 2.2, it may be seen that in an excess of carbon dioxide, without water, the methane conversion is low and little carbon dioxide is converted under these conditions. With increasing frequency, keeping power constant at 11 W, the current is nearly constant while the power factor decreased as the low side voltage increased. The power factor decreased with increasing frequency due to the lag between current and voltage waveforms due to the capacitive nature of the reactor system. Frequency affects not only the electrical parameters but also affects conversion and product distribution as well as energy consumption. At these studied conditions, the maximum conversion of methane and carbon dioxide were found at 400 Hz and consequently the lowest power consumption was also found at this frequency. H_2/CO ratio was constant at 1.3, however, the product distribution changed with frequency. At 400 Hz, CO/C_2 ratio was highest because of decreasing of ethane and ethylene selectivities.

In the last column of Table 2.2, with addition of water, much higher conversions of both carbon dioxide and methane are achieved. Adding water provides more reactive H, OH, and O radicals in the reaction zone. The reactor could be operated at higher power to obtain higher conversion since these radicals inhibit and remove carbon formation. The net energy consumption (eV/molecule of carbon converted) was lower significantly despite 50 percent dilution of carbon dioxide and methane by the water. In addition, H, OH, and O radicals initiate methyl radical formation (Reactions 8-10) resulting in increased methane conversion and decreased energy consumption. H_2 and H produced from dissociation of water (Reactions 6-7). Little C_2 formation occurs evidently due to dehydrogenation and oxidation of methane such that coupling is inhibited. Most of the C from methane and carbon dioxide form carbon monoxide rather than C_2 products as suggested by the high CO/C_2 ratio. Simultaneous carbon dioxide and steam reforming produces higher methane conversions and CO/C_2 ratio than only steam reforming (Table 2.1) or carbon dioxide reforming (Table 2.2).

Table 2.2 Carbon dioxide reforming of methane with/without water-vapor at a 3:1 CO_2/CH_4 ratio.

CO_2/CH_4	3	3	3	3
Water-vapor (%)	0	0	0	50
Low side Voltage (V)	57	68	79	82
Frequency (Hz)	300	400	500	400
Power (W)	11	11	11	14
Power Factor	0.56	0.48	0.42	0.39
Current (A)	0.35	0.34	0.33	0.44
CH_4 conversion (%)	12	19	14	53
CO_2 conversion (%)	2	4	2	20
S_{CO} (%)	63	53	48	89
S_{C2H6} (%)	14	6	12	0
S_{C2H4} (%)	14	9	13	1
S_{C2H2} (%)	19	18	15	5
S_{total} (%)	110	86	88	95
Energy consumption (eV/m_C)	41	21	33	15
H_2/CO	1.3	1.3	1.3	0.6
CO/C_2	2.7	3.2	2.4	27.5

Oxygen species from decomposition of water has a negative effect on C_2 hydrocarbon formation because the newly formed hydrocarbons are still in excited states and then further to be oxidized with oxygen. In addition, decreasing CH_X concentration with water in the feed stream, makes the coupling of methane less favorable. The H_2/CO ratio drop from 1.3 to 0.6 when the system was operated at 50% of water in the feed stream, even though there is more H atom in the feed gas. The result probably reflects using high power, H from methane and water reform water.

3.4 Effect of Power and Water-Vapor on Carbon Dioxide Reforming of Methane with Water-Vapor

At a CO_2/CH_4 ratio of 5.1, methane conversion is substantially increased with a more modest increase in carbon dioxide conversion with increasing power, but there are no significant changes in methane and carbon dioxide conversions with more water content in the feed, as shown in Table 2.3.

Table 2.3 Effect of power and water-vapor on carbon dioxide reforming of methane with water at a 5:1 CO_2/CH_4 ratio.

CO_2/CH_4	5	5	5
Water-vapor (%)	30	30	50
Low side Voltage (V)	62	75	79
Frequency (Hz)	300	300	400
Power (W)	11	13	14
Power Factor	0.43	0.35	0.43
Current (A)	0.41	0.50	0.41
CH_4 conversion (%)	51	57	58
CO_2 conversion (%)	13	17	18
S_{CO} (%)	85	86	100
S_{C2H6} (%)	0	0	0
S_{C2H4} (%)	2	2	0
S_{C2H2} (%)	13	10	3
S_{total} (%)	100	98	103
Energy consumption (eV/m_C)	12	12	17
H_2/CO	0.5	0.4	0.4
CO/C_2	11.1	15.0	68.8

With less water, at 30%, the energy consumption per molecule of carbon converted was substantially reduced compared to 50% water. One of the factors is the dilution and therefore lower throughput of methane at the same power level. As previously mentioned, the radicals from the dissociation of water abstract hydrogen from methane to form methyl radicals resulting in increasing methane conversion. However, a greater number of oxygen radicals could speed up the oxidation reaction to produce carbon dioxide, carbon monoxide, and water. For this reason, some input energy is used to convert recovered carbon dioxide so energy consumption per molecule of carbon converted increased with increasing water from 30% to 50%. Also, there is a substantial suppression of C_2 production with increased water content. Consequently, CO/C_2 ratio was very high (~68.8%) at 50% water-vapor in the feed gas. This result is similar to the results in Table 2.2. The H_2/CO ratio is nearly constant at 0.4 over these three conditions

3.5 Effect of Power and Frequency on Carbon Dioxide Reforming of Methane with Water

The results at the stoichiometric CO_2/CH_4 ratio of 1:1, 50% water-vapor and different frequencies are shown in Table 2.4. Increased power at the 1:1 CO_2/CH_4 ratio shows increased conversion except when the frequency is increased. The increase in frequency essentially "detunes" the system, reducing the power factor and the power actually applied to the plasma. Power was actually measured on the low voltage side and therefore included all high voltage system losses. The system designed to properly match impedances and operated at a high power could significantly lower the real power consumption from that reported here.

Table 2.4 Effect of power and frequency on carbon dioxide reforming of methane with water at a 1:1 CO_2/CH_4 ratio.

CO_2/CH_4	1	1	1	1
Water-vapor (%)	50	50	50	50
Low side Voltage (V)	57	66	88	97
Frequency (Hz)	300	300	400	600
Power (W)	11	13	14	14
Power Factor	0.54	0.45	0.34	0.40
Current (A)	0.36	0.43	0.47	0.36
CH_4 conversion (%)	41	44	47	30
CO_2 conversion (%)	20	21	21	12
S_{CO} (%)	56	60	56	72
S_{C2H6} (%)	2	1	1	3
S_{C2H4} (%)	5	5	5	5
S_{C2H2} (%)	23	24	26	21
S_{total} (%)	86	90	88	101
Energy consumption (eV/m_C)	11	12	12	20
H_2/CO	1.9	1.9	1.9	1.7
CO/C_2	3.9	4.1	3.5	4.9

3.6 Effect of CO_2/CH_4 Ratio on Carbon Dioxide Reforming of Methane with Water

Table 2.5 shows the effect of CO_2/CH_4 ratio on carbon dioxide reforming with water. The methane conversion increased with increasing CO_2/CH_4 ratio while carbon dioxide conversion was constant because of the decreasing methane partial pressure. Energy consumption per carbon converted is lower due to decreased carbon dioxide dilution since methane conversion is the higher of the two. The lower CO_2/CH_4 ratio results in greater C_2 production from the coupling reaction of methane since a decrease in CO_2/CH_4 ratio increases the probability of a methyl radical reacting with another methyl radical. C_2's may be undesirable components of synthesis gas, but the olefinic nature of those produced here are reactive on Fischer Tropsch catalyst systems and therefore may be suitable for feeds to a Fischer Tropsch Synthesis Reactor. The

H_2/CO ratio is close to that desired for Fischer Tropsch or methanol synthesis and may be controllable by altering the water content.

Table 2.5 Effect of CO_2/CH_4 ratio on carbon dioxide reforming of methane with water at 50% water-vapor.

CO_2/CH_4	1	3	5
Water-vapor (%)	50	50	50
Low side Voltage (V)	88	82	79
Frequency (Hz)	400	400	400
Power (W)	14	14	14
Power Factor	0.34	0.39	0.43
Current (A)	0.47	0.44	0.41
CH_4 conversion (%)	47	53	58
CO_2 conversion (%)	21	20	18
S_{CO} (%)	56	89	100
S_{C2H6} (%)	1	0	0
S_{C2H4} (%)	5	1	0
S_{C2H2} (%)	26	5	3
S_{total} (%)	88	95	103
Energy consumption (eV/m_C)	12	15	17
H_2/CO	1.9	0.6	0.4
CO/C_2	3.5	27.5	68.8

In high temperature catalytic steam reforming of methane, the endothermic heat of reaction must be provided at quite high temperatures with very intense heat fluxes. Although the direct fired furnaces used for this are quite efficient (>90%), they are quite expensive including the cost of heat recovery systems. A plasma discharge reactor system uses electricity to drive the reaction and can be assumed to have an efficiency no greater than that of the power generation system (~60% for modern combined cycle combustion turbine plants). However, for the low temperature plasma, little energy is expended in gas heating and heat recovery systems are not needed. Thus, for the plasma system, somewhat higher energy consumption maybe offset by simple process operation and lower cost for investment. This could be true especially for relatively small scale plants, where fuel gas is inexpensive, or where excess (off peak) power generation is available.

CHAPTER IV

CONCLUSIONS

Carbon dioxide combined with steam reforming at moderate conversion levels has been demonstrated at near ambient conditions with moderate power consumption. Under most conditions, carbon formation was not an operational problem. If long term operation with high conversions can be demonstrated, a process can be envisaged wherein the cost and efficiency of using electricity to drive the reaction is counter-balanced by lower costs and simpler operation (without oxygen). For smaller resources and more remote locations, these tradeoffs may be highly advantageous. Whether there is a net reduction in carbon dioxide impact compared to more conventional reforming/partial oxidation synthesis gas generation processes can only be determined by a detailed life cycle analysis and not simply by the apparent reaction stoichiometry.

CHAPTER V

OUTPUT FROM THE PROJECT

5.1 Paper published in the international journal

Author name : K. Supat, S. Chavadej, L. L. Lobban and R. G. Mallinson

Title name : Combined Carbon Dioxide and Steam Reforming with Methane in Low Temperature Plasmas

Journal name : ACS Book (in press)

5.2 Presentation in the international conference

Author name : K. Supat, S. Chavadej, L. L. Lobban and R. G. Mallinson

Title name : Carbon Dioxide Reforming with Methane in Low Temperature Plasma

Conference name : The 223rd ACS National Meeting, Orlando, Florida, USA
Presented on 7-11 April 2000

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APPENDICES

1. Manuscript submitted to the 223rd ACS National Meeting, Orlando, Florida, USA presented on 7-11 April 2000 on the topic of Carbon Dioxide Reforming with Methane in Low Temperature Plasma.

2. Manuscript submitted to ACS book on the topic of Combined Carbon Dioxide and Steam Reforming with Methane in Low Temperature Plasmas (in process).

CARBON DIOXIDE REFORMING WITH METHANE IN LOW TEMPERATURE PLASMAS

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Introduction

With increasing population and rapid technology development, it is possible that we have begun to encounter alteration of the climate. Greenhouse gases, that include carbon dioxide, methane, ozone, halocarbons and nitrous oxide, to a significant extent come from the combustion of fossil fuels (coal, oil, and natural gas) for power generation and transportation. A potentially useful reaction for reducing the impact of carbon dioxide (reducing net emissions), a major component in many natural gas resources, especially in Asia, is carbon dioxide reforming with methane (reaction 1) for production of synthesis gas (carbon monoxide and hydrogen) at a lower H_2/CO ratio compared to steam reforming of methane (reaction 2), which is the conventional process for synthesis gas production. However, as with steam reforming, the highly endothermic reaction requires significant high temperature (ca. 800 °C) energy input that is usually provided by combustion that releases CO_2. Also, the 1:1 H_2/CO ratio produced from CO_2 reforming requires, for GTL applications, the use of the water gas shift reaction, in which much of the potential net consumption of CO_2 is lost. The alternative is to combine CO_2 reforming with steam reforming and its similar low net CO_2 reduction due to combustion to provide the required heat of reaction. Thus any net reduction of CO_2 impact from the process must be compared with the partial oxidation or combined/autothermal reforming which are exothermic or self heating, but require the production of oxygen that is itself energy intensive.

$$CH_4 + CO_2 \longrightarrow 2\,CO + 2\,H_2 \qquad \Delta H = 247.0\ kJ\ mol^{-1} \qquad (1)$$

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2 \qquad \Delta H = 229.7\ kJ\ mol^{-1} \qquad (2)$$

Therefore, rather than considering the net CO_2 reduction as the driver, other factors must be considered. For example, The previously mentioned high CO_2 natural gas resources may be stranded by the high cost of CO_2 removal, which may be reduced or eliminated by use of CO_2 reforming. Additionally, the possible lower capital investment and operating costs due to the elimination of the requirement for oxygen makes consideration of this technology worthwhile. However, a major problem with CO_2 reforming to this point in time is the deactivation of the catalyst due to carbon deposition (reaction 3 and 4) at the desired reaction conditions.

$$CH_4 \longrightarrow C + 2H_2 \qquad \Delta H = 75\ kJ\ mol^{-1} \qquad (3)$$

$$2CO \longrightarrow C + CO_2 \qquad \Delta H = -171\ kJ\ mol^{-1} \qquad (4)$$

So far, no effective commercial catalyst exists which can operate without carbon formation [1]. Therefore, solving these problems to find ways to operate this process at milder reaction conditions is of great interest.

In this work, a low temperature plasma reactor was used to facilitate this reaction by itself and in combination with steam, at low temperatures. This has been shown to be possible in other methane conversion studies without carbon dioxide, such as helping in the conversion of methane over Sr/La_2O_3 [2] and other materials. The disadvantage of using electrical energy, that at best may only be about 60 percent efficient, may be offset by process simplicity and cost, lower carbon formation and less excess energy that must be recovered and utilized only with considerable cost.

A plasma is a quasineutral gas consisting of charged and neutral gas molecules with a collective behavior in which the charged molecules follow the path of the electric field. It is in equilibrium when the kinetic energy of the charged particles and neutral species are the same. The non-thermal, also called cold, plasma, and its non-equilibrium properties, high electron temperature and low bulk gas temperature, provide the capability for initiating chemical reactions at low temperature and with lower energy input.

Corona discharge and dielectric barrier discharge (DBD) techniques are two of the commonly used methods for producing non-equilibrium plasmas at atmospheric pressure [3], [4], [5]. Because the corona is particularly easy to establish, it has had wide application in a variety of processes such as electrostatic precipitation, electro-photography and also synthesis of chemicals [3]. The electron energy, which corresponds to the electron temperature, is restricted to less than 6 eV in the corona discharge [6]. These relatively low-energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than 12 eV [7], but high enough to dissociate CH_4 and CO_2 molecules with dissociation energies of 4.5 and 5.5 eV, respectively (reaction 5 and 6) [1].

$$e^- + CH_4 \longrightarrow CH_3 + H + e^- \qquad (5)$$

$$e^- + CO_2 \longrightarrow CO + O + e^- \qquad (6)$$

The utilization of non-equilibrium plasma techniques for carbon dioxide reforming with methane has been studied in the dielectric barrier discharge. The combination of solid catalysts with a dielectric-barrier discharge was studied for carbon dioxide reforming of methane. It is shown that the use of a catalytic coating in the discharge can have a promoting effect on the plasma chemistry and the use of the ceramic foams improved the temperature and lowered the undesired temperature increase [4]. The dielectric barrier discharge has also been used to investigate the effect of a non-equilibrium discharge on the production of synthesis gas from two major greenhouse gases carbon dioxidand methane. A pronounced synergistic effect caused by free radical reactions was observed using these two gases simultaneously with a minimum required specific energy of 40 eV/molecule for the production of syngas and the highest energy efficiency (electric energy converted to chemical energy in the syngas) reached so far was about 7%[1]. The effect of a third body (helium) was also investigated in the DBD for carbon dioxide reforming [8].

Experimental

The flow rate of feed gases, methane and carbon dioxide, were controlled by a set of mass flow controllers supplied by Porter Instrument, Inc. All experiments were carried out at atmosphere pressure. The feed gases were introduced downward through the reactor and analyzed on-line by a Carle AGC 400 gas chromatograph, with thermal conductivity detector. To provide the water vapor in the feed, the feed gas was bubbled through a water saturation system in a water bath maintained at the temperature needed to provide the desired vapor pressure of water. All inlet and exit lines were heat traced and the reactor tube was placed in a heater and maintained at 100°C. The exhaust gas from the reactor was introduced into a condenser cooled by a mixture of dry ice and acetone that was used to remove the condensable products. The power supply unit consisted of an AC power supply for converting domestic AC power 120V, 60 Hz, using a function generator for varying the frequency in the range of 300 to 600 Hz with a sinusoidal waveform. The output was then transmitted to a high voltage alternating current (HVAC) transformer. The HVAC could step up the low side voltage to the high side voltage by nominal factor of 125 at 60 Hz. This factor may not be constant with changes in frequency due to changes in power factor because of the capacitive nature of the reactor system. The discharge occurred in a quartz tube with an i.d. of 7 mm between two stainless steel electrodes. The upper wire electrode is centered axially within the reactor tube, while the lower electrode is a circular plate with four holes to allow gas to pass through the reactor and is positioned perpendicular to the reactor axis

For this system, the conversions are defined as:

Conversion of methane = (moles of CH_4 consumed/moles of CH_4 introduced) x 100 %

Conversion of carbon dioxide = (moles of CO_2 consumed/moles of CO_2 introduced) x 100 %

H_2/CO mole ratio = moles of H_2 produced/moles of CO produced

CO/C_2 mole ratio = moles of CO produced/moles of ethane, ethylene and acetylene produced

In some cases, at lower methane conversions, the product material balances could be below 80%, however in most cases the product carbon balance was in the 80-90% range. Water was not quantified.

Results and Discussion

In Table 1, It may be seen that in an excess of CO_2, without water, the methane conversion is low and little CO_2 is converted even as power is substantially increased. In the last column with addition of water, much higher conversion of both CO_2 and methane is achieved at otherwise similar conditions. Power is somewhat higher, but eV/mol of carbon converted is lower despite a 50 percent dilution of CO_2 and CH_4 by the water. With the excess CO_2, little C_2 formation occurs and the H_2/CO is quite low.

At a CO_2:CH_4 ratio of 5:1, methane conversion is substantially increased with a more modest increase in CO_2 conversion. With less water, at 30 %, energy consumption per C converted is substantially reduced compared to 50 % water. Also noticeable is a substantial suppression of C_2 production with increased water content. At 30 percent water in the feed, are increases in both conversions but hydrogen production appears to be significantly reduced.

The results at the stoichiometric CO_2:CH_4 ratio of 1:1 and 50% water vapor are shown in Table 3. The conversions are similar to those at the 3:1 ratio with the same power and water content, but Energy consumption per C converted is lower due to decreased CO_2 dilution since methane conversion is the higher of the two. Increased power at 1:1 ratio shows increased conversion except when the frequency is increased. The increase in frequency essentially "detunes" the system, reducing the power factor and the power actually applied to the plasma. Power is actually measured on the low voltage side and therefore includes all high voltage system losses. A system designed to properly match impedances and operate at a high power could significantly lower the real power usage over that reported here. The lower CO_2:CH_4 ratio results in greater C_2 production. C_2's may be undesirable components of synthesis gas.

Table 1. Effect of Power and Water on CO_2 Reforming at a 3:1 CO_2: CH_4 Ratio

Flowrate (sccm)	100	100	100	100
CO2:CH4	3	3	3	3
% vapor	0	0	0	50
Gas gap (cm)	1	1	1	1
Low side Voltage(V)	57	68	79	62
Frequency	300	400	500	400
Power (W)	11	11	11	14
Power Factor	0.56	0.48	0.42	0.78
Current (Amp)	0.35	0.34	0.33	0.29
X_{CH4}	11.5	19.2	14.0	34.4
XCO_2	1.5	4.1	2.0	13.0
S_{CO}	63.4	52.9	47.8	99.9
S_{H2}	-	-	-	-
S_{C2H6}	13.8	5.9	11.6	1.0
S_{C2H4}	13.6	9.1	13.0	1.0
S_{C2H2}	18.8	17.6	14.9	4.5
S_{total}	109.6	85.5	87.3	106.3
eV $m_{(CO2+CH4)}$	41.4	21.0	33.0	23.3
H2/CO	1.28	1.26	1.31	0.65
CO/C2	2.74	3.24	2.42	31.07

Table 2. Effect of Power and Water on CO_2 Reforming with Water at a 5:1 CO_2:CH_4 Ratio

Flowrate (sccm)	100	100	100
CO2:CH4	5	5	5
% vapor	30	30	50
Gas gap (cm)	1	1	1
Low side Voltage(V)	62	75	79
Frequency	300	300	400
Power (W)	11	13	14
Power Factor	0.43	0.35	0.43
Current (Amp)	0.41	0.50	0.41
X_{CH4}	51.1	57.4	58.1
XCO_2	13.2	17.1	18.2
S_{CO}	85.3	86.4	100.2
S_{H2}	-	-	-
S_{C2H6}	0.0	0.0	0.0
S_{C2H4}	2.3	1.6	0.0
S_{C2H2}	13.2	9.9	2.9

S_{total}	100.8	97.9	103.1
eV/$m_{C(CO2-CH4)}$	12.1	11.7	17.1
H2/CO	5.00	0.44	0.41
CO/C2	11.05	14.97	68.83

but the olefinic nature of those produced here are reactive on Fischer Tropsch catalyst systems and therefore may be suitable for feeds to a Fischer Tropsch Synthesis Reactor. The H_2/CO ratio is close to that desired for Fischer Tropsch or methanol and may be controllable by altering the water content.

Table 3. Effect of Power on CO_2 Reforming with Water at a 1:1 CO_2: CH_4 Ratio

Flowrate (sccm)	100	100	100	100
CO2:CH4	1	1	1	1
% vapor	50	50	50	50
Gas gap (cm)	1	1	1	1
Low side Voltage(V)	57	66	88	97
Frequency	300	300	400	600
Power (W)	11	13	14	14
Power Factor	0.54	0.45	0.34	0.40
Current (Amp)	0.36	0.43	0.47	0.36
X_{CH4}	40.5	44.3	47	30
XCO_2	19.6	20.9	21	12
S_{CO}	55.5	60.2	56	72
S_{H2}	-	-	-	-
S_{C2H6}	1.5	1.4	1	3
S_{C2H4}	4.6	4.5	5	5
S_{C2H2}	22.7	23.8	26	21
S_{total}	84.3	89.9	88	101
eV/$m_{C(CO2-CH4)}$	11.0	12.0	12.3	19.7
H2 CO	1.90	1.85	1.9	1.7
CO/C2	3.85	4.05	3.5	4.9

Table 4. Water Gas Shift Reaction Pathway

Flowrate (sccm)	100	100
CO2:CH4	50%CO	50%CO_2
% vapor	50	50
Gas gap (cm)	1	1
Low side Voltage(V)	63	85
Frequency	600	400
Power (W)	7	10
Power Factor	0.49	0.27
Current (Amp)	0.23	0.44
X_{CH4}	X_{CO} = 6.03	0
XCO_2	0	1
S_{CO}	-	112
S_{H2}	-	-
S_{C2H6}	0	0
S_{C2H4}	0	0
S_{C2H2}	S_{CO_2} = 105.05	0
S_{total}	105	112
eV/$m_{C(CO2-CH4)}$	34.6	352.7
H2/CO	H_2/CO_2 = 0.87	0.0
CO/C2	-	-

Lastly, in Table 4, results of reacting with CO or CO_2 with water are shown. CO_2 and water are essentially unreactive under the conditions of this experiment, where of course both species are strongly favored by thermodynamics. CO and water or converted to some extent with the expected production of hydrogen and CO_2. Power consumption is high under these condtions, but a lower value might be feasible under optimal condtions.

Conclusions

CO_2 combined with steam reforming at moderate conversion levels has been demonstrated at near ambient conditions with moderate power consumption. Under most conditions, carbon formation was not an operational problem. If long term operation with high conversions can be demonstrated, a process can be envisaged wherein the cost and efficiency of using electricity to drive the reaction is counter-balanced by lower costs and simpler operation (without oxygen). For smaller resources and more remote locations, these tradeoffs may be highly advantageous. Whether there is a net reduction in CO_2 impact compared to more conventional reforming partial oxidation syn gas generation processes can only be determined by a detailed life cycle analysis and not simply by the reaction equations.

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RESERVE THIS SPACE

Combined Carbon Dioxide and Steam Reforming with Methane in Low Temperature Plasmas

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The combination of carbon dioxide reforming and steam reforming with methane is investigated in a corona discharge reactor with moderate power consumption. The plasma is used to overcome the energy barrier of these two endothermic reactions instead of high temperature catalytic processes. Simultaneous carbon dioxide and steam reforming produces higher methane conversions and CO/C_2 ratios than only steam reforming or carbon dioxide reforming. The H_2/CO ratio of 1.9:1 is close to that desired for Fischer Tropsch or methanol synthesis was achieved at a CO_2/CH_4 ratio of 1:1 with 50% water-vapor in the feed stream. In this condition, the energy consumption is about 12 eV/molecule of carbon converted.

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Using electricity to drive the reaction at low temperature is counter-balanced by lower costs and simpler operation.

With increasing population and rapid technology development, it is possible that we have begun to encounter alteration of the climate. .Greenhouse gases that include carbon dioxide, methane, ozone, halocarbons and nitrous oxide, to a significant extent come from the combustion of fossil fuels (coal, oil, and natural gas) for power generation and transportation. A potentially useful reaction for reducing the impact of carbon dioxide (reducing net emissions), a major component in many natural gas resources, especially in Asia, is carbon dioxide reforming with methane (Reaction 1) for production of synthesis gas (carbon monoxide and hydrogen) at a lower H_2/CO ratio compared to steam reforming of methane (Reaction 2), which is a major conventional process for synthesis gas production. A typical industrial steam reformer operates at 1,120-1,170 K and 15-30 atm over a Ni/Al_2O_3 catalyst (1). However, as with steam reforming, the highly endothermic reaction requires significant high temperature energy input that is usually provided by combustion that releases carbon dioxide. Also, the 1:1 H_2/CO ratio produced from carbon dioxide reforming requires, for GTL applications, the use of the water gas shift reaction, in which much of the potential net consumption of carbon dioxide is lost. However, a major problem with carbon dioxide reforming to this point in time is the deactivation of the catalyst due to carbon deposition (Reactions 3 and 4) at the desired reaction conditions.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ mol}^{-1} \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206 \text{ kJ mol}^{-1} \qquad (2)$$

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 75 \text{ kJ mol}^{-1} \qquad (3)$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H = -172 \text{ kJ mol}^{-1} \qquad (4)$$

So far, There is no effective commercial catalyst which can operate without carbon formation (2). The alternative is to combine carbon dioxide reforming with steam reforming. A thermodynamics study has shown that the presence of water in carbon dioxide reforming allows increased methane conversion (3) and probably decreased carbon formation at a specific CO_2/CH_4 ratio. Moreover, for several feed ratios of CH_4:CO_2, the desired H_2/CO ratio at equilibrium is controllable by the amount of water added in feed stream, for example, the desired ratio of H_2/CO of 1:1 can be obtained from a Terrell natural gas by using up to 3.28% of water in the feed (3). Both carbon dioxide reforming and steam reforming have similar low net carbon dioxide reduction due to combustion needed to provide the required heat of reaction. Thus any net reduction of carbon dioxide impact from the process must be compared with partial oxidation or combined/autothermal reforming which are exothermic or self heating, but require the production of oxygen that is itself energy intensive. Therefore, rather than considering the net carbon dioxide reduction as the driver, other factors must be considered. For example, high carbon dioxide in natural gas resources may be stranded by the high cost of carbon dioxide removal, which may be reduced or eliminated by use of carbon dioxide reforming. Additionally, the possible lower capital investment and operating costs due to the elimination of the requirement for oxygen makes consideration of this technology worthwhile. Due to the fact that carbon dioxide reforming and steam reforming are endothermic reactions, the high reaction temperature requires an intensive energy input and a high operating cost. One may uses non-equilibrium plasma to reduce energy cost instead of thermal process.

The non-thermal, also called cold, plasma, and its non-equilibrium properties, high electron temperature and low bulk gas temperature, provide the capability for initiating chemical reactions at low temperature and potentially with low energy input. The non-equilibrium plasma is used to overcome the energy barrier to start the reaction by promoting radical production (4).

Corona discharge and dielectric barrier discharge (DBD) techniques are two of the commonly used methods for producing non-equilibrium plasmas at atmospheric pressure (5). The utilization of the non-equilibrium plasma techniques for carbon dioxide reforming with methane has been studied in the dielectric barrier discharge (2, 6-8).

The spectroscopic characteristic of a plasma created in a methane and carbon dioxide mixture by a high-voltage, steep front-voltage, very-short-pulse triggered dielectric barrier discharge in a tubular cell was investigated. The very steep front voltage ($>10^{12}$ V/s) allowed the reactor to operate at higher reduced field values (E/n) than in conventional DBD systems. To confirm the properties of the non-equilibrium plasma, it was shown that the temperature inside the streamers was around 3,000 K and the mean gas temperature in the active volume was close to room temperature (6).

The effects of CO_2/CH_4 ratio and adding helium to a 1:1 CO_2/CH_4 ratio feed stream were studied. The results indicated that CO_2/CH_4 ratio strongly affected the results. Increasing the partial pressure of carbon dioxide from a 1:2 to 1:1

CO_2/CH_4 ratio caused increased carbon dioxide conversion to carbon monoxide but reduced the ethane and hydrogen selectivities. A further increase in the CO_2/CH_4 ratio from 1:1 to 2:1 caused an increase in ethane and hydrogen selectivities. Despite lowering methane partial pressure, helium acts as a third body in enhancing methane conversion and carbon monoxide selectivities (7).

A numerical simulation was performed to investigate the conversion of methane and carbon dioxide to synthesis gas in a DBD reactor. Using curve-fitting, the H_2/CO ratio can be presented as a simple function of a mixing ratio of CH_4/CO_2 which can be approximated over a wide range. Specific electric energy, gas pressure, and temperature hardly influence syngas composition (2).

The combination of solid catalysts with a dielectric-barrier discharge also has been studied for carbon dioxide reforming of methane. It was shown that the nickel and the nickel-calcium coated foams showed nearly identical activities for the reforming reaction in the discharge in the temperature range of 40 - 230 °C and gave significantly higher carbon monoxide production than the rhodium coated catalyst and the uncoated foam. The reaction was operated over the stoichiometric ratio at a CO_2/CH_4 ratio of 3:1 to minimize hydrocarbon formation. After the reaction, small amount of carbon or carbonaceous deposits were found on the foams (8).

Because the corona discharge is particularly easy to establish, it has had wide application in a variety of processes such as electrostatic precipitation, electro-photography, static control in semiconductor manufacture, ionization instrumentation, destruction of toxic compounds, generation of ozone, and synthesis of chemicals (9).

In this work, a corona discharge reactor was used to facilitate carbon dioxide reforming by itself and in combination with steam at low temperatures. This has been shown to be possible in other methane conversion studies without carbon dioxide, such as helping in the conversion of methane over Sr/La_2O_3 (10) and other materials (11). The disadvantage of using electrical energy, that at best may only be about 60 percent efficient, may be offset by process simplicity and cost, lower carbon formation and less excess energy that must be recovered and utilized only with considerable cost.

Experimental

The flow rates of feed gases were controlled by a set of mass flow controllers supplied by Porter Instrument, Inc. Water-vapor was introduced into the reactor by passing the feed gases through a water-bath of which the temperature was controlled to adjust the concentration of water-vapor in the feed gas mixture. The feed gases were well mixed and then flowed downward through the reactor. The reactor temperature was controlled to be constant 100 ° C to avoid water condensation during reaction. All the experiments were operated at atmospheric pressure. The feed gases and the exhaust gases from the reactor were introduced into two condensers in series cooled by ice water that were used to remove the condensable products as well as water and then analyzed on-line by a Carle AGC 400 gas chromatograph with thermal conductivity detector. However, no organic products were collected from the condensers when analyzed with a Varian 3300 GC with a Porapak Q Column. The power supply unit consisted of an AC power supply for converting domestic AC power 120 V, 60 Hz, using a function generator to vary the frequency in the range of 300 to 600 Hz with a sinusoidal waveform. The output was then transmitted to a high voltage alternating current (HVAC) transformer. The HVAC transformer could step up the low side voltage to the high side voltage by a nominal factor of 125 at 60 Hz. This factor may not be constant with changes in frequency due to changes in the power factor because of the capacitive nature of the reactor system. The discharge occurred between two stainless steel electrodes in a quartz tube with an inside diameter of 7 mm. The gap distance between these two electrodes was 1 cm. The feed gas flow rate was the same for every experiment at 100 sccm corresponding to a residence time of 0.23 s. The upper wire electrode was centered axially within the reactor tube, while the lower electrode was a circular plate with holes to allow gas to pass through the reactor and positioned perpendicular to the reactor axis. An Extech power analyzer was used to measure the power, power factor, current, frequency, and voltage at the low side of the power circuit.

For this system, the energy consumption for conversion of carbon in the feed gas consisting of methane and carbon dioxide is given in units of electron-volt/molecule of carbon converted (eV/m_C). S_X is defined as the selectivity based on converted carbon in both carbon dioxide and methane. S_{total} is defined as the total selectivities of all products which contain C (carbon atom).

All experiments had a carbon balance greater than 84%. Water was not quantified.

Results and Discussion

The electron energy, which corresponds to the electron temperature, is restricted to less than 6 eV in the corona discharge (12). These relatively low-energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than 12 eV (13), but high enough to dissociate carbon dioxide molecules with dissociation energies of 5.5 eV (Reaction 5) (2, 5, 14).

$$e^- + CO_2 \rightarrow CO + O + e^- \qquad (5)$$

H_2O also requires only a relatively low electron energy to be dissociated to produce O, H and OH radicals as shown in Reactions 6 and 7 (15) :

$$e^- + H_2O \rightarrow O^- + H_2 \qquad (6)$$

$$e^- + H_2O \rightarrow OH^- + H \qquad (7)$$

These radicals, H, OH and O, further abstract hydrogen from methane to form methyl radical (CH_3) leading to a significant rate of methane conversion in the corona discharge (Reactions 8-10).

Methyl radical formation :

$$CH_4 + O \rightarrow CH_3 + OH \qquad (8)$$

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad (9)$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (10)$$

These methyl radicals react further to either combine with another CH_3 to form ethane (Reaction 11) or break down into CH_2, CH and C and subsequently form ethylene, acetylene and carbon oxides (16). Ethane can be dehydrogenated to form ethylene and acetylene and ethylene can be dehydrogenated to form acetylene. These reaction pathways were also observed in the conversion of methane via microwave plasmas (17). The coupling of hydrogen radicals forms hydrogen. Beyond these main reactions, there maybe many contributing reaction pathways in the corona discharge environment. Some of the possible ethane, ethylene, acetylene and hydrogen formation reactions are shown in Reactions 11-39. Water may be formed in the discharge via Reactions 40-43.

Ethane formation :

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (11)$$

$$CH_4 + CH_2 \rightarrow C_2H_6 \tag{12}$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \tag{13}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 \tag{14}$$

Ethylene formation :

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{15}$$

$$C_2H_6 \rightarrow CH_3 + CH_3 \tag{16}$$

$$CH_3 + CH_3 \rightarrow C_2H_4 + H_2 \tag{17}$$

$$CH_3 + CH_2 \rightarrow C_2H_4 + H \tag{18}$$

$$CH_2 + CH_2 \rightarrow C_2H_4 \tag{19}$$

$$CH_3 + CH_3 \rightarrow C_2H_5 + H \tag{20}$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \tag{21}$$

$$C_2H_6 + CH_3 \rightarrow CH_4 + C_2H_5 \tag{22}$$

$$C_2H_5 + H \rightarrow CH_3 + CH_3 \tag{23}$$

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$$C_2H_5 + H \rightarrow C_2H_4 + H_2 \quad (24)$$

Acetylene formation :

$$C_2H_4 \rightarrow C_2H_2 + H_2 \quad (25)$$

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \quad (26)$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 \quad (27)$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \quad (28)$$

$$CH + CH \rightarrow C_2H_2 \quad (29)$$

$$CH_2 + CH \rightarrow C_2H_2 + H \quad (30)$$

CO_X formation :

$$CH_3 + O \rightarrow HCHO + H \quad (31)$$

$$HCHO + O \rightarrow OH + CHO \quad (32)$$

$$CHO + O \rightarrow OH + CO \quad (33)$$

$$CHO + O \rightarrow CO_2 + H \quad (34)$$

$$HCHO + H \rightarrow H_2 + CHO \tag{35}$$

$$CHO + H \rightarrow H_2 + CO \tag{36}$$

$$HCHO + O\dot{H} \rightarrow CHO + H_2O \tag{37}$$

$$CHO + \dot{O}H \rightarrow CO + H_2O \tag{38}$$

Hydrogen formation :

$$2H \rightarrow H_2 \tag{39}$$

Water formation:

$$OH + H \rightarrow H_2O \tag{40}$$

$$OH + C_xH_y \rightarrow H_2O + C_xH_{y-1} \tag{41}$$

$$2H + O \rightarrow H_2O \tag{42}$$

$$H_2 + O \rightarrow H_2O \tag{43}$$

Moreover, the radicals of H, OH, and O generated from dissociation of water are essential ingredient for the inhibition and removal of carbon deposits which have a negative effect on gas discharges, shown in Reactions 44 and 45 (18).

$$C_{(S)} + H \rightarrow CH \tag{44}$$

$$CH_{(S)} + H \rightarrow CH_2 \qquad (45)$$

In Table I, results of a feed stream of 50% methane or carbon dioxide or carbon monoxide reacted with 50% water are shown. Many products, CO, CO_2, C_2H_6, C_2H_4, C_2H_2, and H_2, were produced from methane with water but C_2 products were not produced from carbon dioxide with water or from carbon monoxide with water. Methane and water in the corona discharge not only steam reforms methane but other reactions also occur. The H_2/CO ratio is quite high; more than the stoichiometric ratio for steam reforming. In the industrial catalytic process, the syngas ratio (H_2/CO) obtained with steam reforming is higher than 3 caused by a surplus of steam (19, 20). High hydrogen production here results from the net dehydrogenation with the formation of C_2 hydrocarbon products and hydrogen also can be produced directly from the dissociation of water in the corona discharge as shown in Reaction 6. Steam reforming of methane in the low temperature plasma environment is an alternative way to produce synthesis gas instead of the conventional process.

Table I. Reactions of methane, carbon dioxide, carbon monoxide with water-vapor

Carbon (%)	50% CH_4	50% CO_2	50% CO
Water-vapor (%)	50	50	50
Low side Voltage (V)	57	85	63
Frequency (Hz)	600	400	600
Power (W)	13	10	7
Power Factor	0.48	0.27	0.49
Current (A)	0.48	0.44	0.23
C conversion (%)	$X_{CH4} = 27$	$X_{CO2} = 1$	$X_{CO} = 6$
S_{CO} (%)	35	112	-
S_{CO2} (%)	1	0	105
S_{C2H6} (%)	5	0	0
S_{C2H4} (%)	8	0	0
S_{C2H2} (%)	39	0	0
S_{total} (%)	88	112	105
Energy consumption (eV/m_C)	14	353	35
H_2/CO_x	$H_2/CO = 4.7$	$H_2/CO = 0.0$	$H_2/CO_2 = 0.9$
CO/C_2	1.4	-	-
CO/O_2	-	2.3	-

Carbon dioxide with water is essentially unreactive under the conditions of this experiment, where of course both species are strongly favored by thermodynamics. Even though methane with water and carbon dioxide with water have the same current, or an equal the number of electrons to initiate reactions, carbon dioxide conversion is much lower than methane conversion. The products were only oxygen and carbon monoxide with a CO/O_2 ratio of 2.3. Carbon monoxide with water is converted to some extent with the expected production of hydrogen and carbon dioxide. The H_2/CO_2 was about 0.9, that is close to the stoichiometric ratio of the water gas shift reaction. Energy consumption of carbon dioxide with water and carbon monoxide with water is very high under these conditions.

Table II. Carbon dioxide reforming of methane with/without water-vapor at a 3:1 CO_2/CH_4 ratio

CO_2/CH_4	3	3	3	3
Water-vapor (%)	0	0	0	50
Low side Voltage (V)	57	68	79	82
Frequency (Hz)	300	400	500	400
Power (W)	11	11	11	14
Power Factor	0.56	0.48	0.42	0.39
Current (A)	0.35	0.34	0.33	0.44
CH_4 conversion (%)	12	19	14	53
CO_2 conversion (%)	2	4	2	20
S_{CO} (%)	63	53	48	89
S_{C2H6} (%)	14	6	12	0
S_{C2H4} (%)	14	9	13	1
S_{C2H2} (%)	19	18	15	5
S_{total} (%)	110	86	88	95
Energy consumption (eV/m_C)	41	21	33	15
H_2/CO	1.3	1.3	1.3	0.6
CO/C_2	2.7	3.2	2.4	27.5

In Table II, it may be seen that in an excess of carbon dioxide, without water, the methane conversion is low and little carbon dioxide is converted under these conditions. With increasing frequency, keeping power constant at 11 W, the current is nearly constant while the power factor decreased as the low side voltage increased. The power factor decreased with increasing frequency due to the lag between current and voltage waveforms due to the capacitive nature of the reactor system. Frequency affects not only the electrical parameters but also affects conversion and product distribution as well as energy consumption. At these conditions, the maximum conversion of methane and carbon dioxide are found at 400 Hz and consequently the lowest power consumption is found at the same frequency. H_2/CO ratio is constant at 1.3, however, the product distribution changes with frequency. At 400 Hz, CO/C_2 ratio is highest because of decreasing of ethane and ethylene selectivities.

In the last column, with addition of water, much higher conversions of both carbon dioxide and methane are achieved. Adding water provides more reactive H, OH, and O radicals in the reaction zone. The reactor could be operated at higher power to obtain higher conversion since these radicals inhibit and remove carbon formation. The net energy consumption (eV/molecule of carbon converted) is lower despite a 50 percent dilution of carbon dioxide and methane by the water. In addition, H, OH, and O radicals initiate methyl radical formation (Reactions 8-10) resulting in increased methane conversion and decreased energy consumption. H_2 and H produced from dissociation of water (Reactions 6-7). Little C_2 formation occurs evidently due to dehydrogenation and oxidation of methane such that coupling is inhibited. Most of the C from methane and carbon dioxide form carbon monoxide rather than C_2 products as suggested by the high CO/C_2 ratio. Simultaneous carbon dioxide and steam reforming produces higher methane conversions and CO/C_2 ratio than only steam reforming (Table I) or carbon dioxide reforming (Table II). Oxygen species from decomposition of water has a negative effect on C_2 hydrocarbon formation because the newly formed hydrocarbons are still in excited states and then further to be oxidized with oxygen. In addition, decreasing CH_X concentration with water in the feed stream, makes the coupling of methane less favorable. The H_2/CO ratio drop from 1.3 to 0.6 when the system was operated at 50 % of water in feed stream, even though there is more H atom in the feed gas. The result probably reflecs using high power, H from methane and water reform water.

At a CO_2/CH_4 ratio of 5:1, methane conversion is substantially increased with a more modest increase in carbon dioxide conversion with increasing power, but there are no significant changes in methane and carbon dioxide conversions with more water content in the feed, as shown in Table III. With less water, at 30%, energy consumption per molecule of carbon converted is substantially reduced compared to 50% water. One of the factors is the dilution and therefore lower throughput of methane at the same power level. As previously mentioned, the radicals from the dissociation of water abstract hydrogen from methane to form methyl radicals resulting in increasing methane conversion. However, a greater number of oxygen radicals could speed up the oxidation reaction to produce carbon dioxide, carbon monoxide, and water. For this reason, some input energy is used to convert recovered carbon dioxide so energy consumption per molecule of carbon converted increases with increasing water from 30% to 50%. Also, there is a substantial suppression of C_2 production with increased water content. Consequently, CO/C_2 ratio is very high (~68.8%) at 50% water-vapor in the feed gas. This result is similar to the results in Table II. The H_2/CO ratio is nearly constant at 0.4 over these three conditions

Table III. Effect of power and water-vapor on carbon dioxide reforming of methane with water at a 5:1 CO_2/CH_4 ratio

CO_2/CH_4	5	5	5
Water-vapor (%)	30	30	50
Low side Voltage (V)	62	75	79
Frequency (Hz)	300	300	400
Power (W)	11	13	14
Power Factor	0.43	0.35	0.43
Current (A)	0.41	0.50	0.41
CH_4 conversion (%)	51	57	58
CO_2 conversion (%)	13	17	18
S_{CO} (%)	85	86	100
S_{C2H6} (%)	0	0	0
S_{C2H4} (%)	2	2	0
S_{C2H2} (%)	13	10	3
S_{total} (%)	100	98	103
Energy consumption (eV/m_C)	12	12	17
H_2/CO	0.5	0.4	0.4
CO/C_2	11.1	15.0	68.8

The results at the stoichiometric CO_2/CH_4 ratio of 1:1 and 50% water-vapor are shown in Table IV. Increased power at the 1:1 CO_2/CH_4 ratio shows increased conversion except when the frequency is increased. The increase in frequency essentially "detunes" the system, reducing the power factor and the power actually applied to the plasma. Power is actually measured on the low voltage side and therefore includes all high voltage system losses. A system designed to properly match impedances and operate at a high power could significantly lower the real power consumption from that reported here.

Table IV. Effect of power on carbon dioxide reforming of methane with water at a 1:1 CO_2/CH_4 ratio

CO_2/CH_4	1	1	1	1
Water-vapor (%)	50	50	50	50
Low side Voltage (V)	57	66	88	97
Frequency (Hz)	300	300	400	600
Power (W)	11	13	14	14
Power Factor	0.54	0.45	0.34	0.40
Current (A)	0.36	0.43	0.47	0.36
CH_4 conversion (%)	41	44	47	30
CO_2 conversion (%)	20	21	21	12
S_{CO} (%)	56	60	56	72
S_{C2H6} (%)	2	1	1	3
S_{C2H4} (%)	5	5	5	5
S_{C2H2} (%)	23	24	26	21
S_{total} (%)	86	90	88	101
Energy consumption (eV/m_C)	11	12	12	20
H_2/CO	1.9	1.9	1.9	1.7
CO/C_2	3.9	4.1	3.5	4.9

Table V shows the effect of CO_2/CH_4 ratio on carbon dioxide reforming with water. The methane conversion increases with increasing CO_2/CH_4 ratio while carbon dioxide conversion is constant because of the decreasing methane partial pressure. Energy consumption per carbon converted is lower due to decreased carbon dioxide dilution since methane conversion is the higher of the two. The lower CO_2/CH_4 ratio results in greater C_2 production from the coupling reaction of methane since a decrease in CO_2/CH_4 ratio increases the probability of a methyl radical reacting with another methyl radical. C_2's may be undesirable components of synthesis gas, but the olefinic nature of those produced here are reactive on Fischer Tropsch catalyst systems and therefore may be suitable for feeds to a Fischer Tropsch Synthesis Reactor. The H_2/CO ratio is close to that desired for Fischer Tropsch or methanol synthesis and may be controllable by altering the water content.

Table V. Effect of CO_2/CH_4 ratio on carbon dioxide reforming of methane with water at 50% water-vapor

CO_2/CH_4	1	3	5
Water-vapor (%)	50	50	50
Low side Voltage (V)	88	82	79
Frequency (Hz)	400	400	400
Power (W)	14	14	14
Power Factor	0.34	0.39	0.43
Current (A)	0.47	0.44	0.41
CH_4 conversion (%)	47	53	58
CO_2 conversion (%)	21	20	18
S_{CO} (%)	56	89	100
S_{C2H6} (%)	1	0	0
S_{C2H4} (%)	5	1	0
S_{C2H2} (%)	26	5	3
S_{total} (%)	88	95	103
Energy consumption (eV/m_C)	12	15	17
H_2/CO	1.9	0.6	0.4
CO/C_2	3.5	27.5	68.8

In high temperature catalytic steam reforming of methane, the endothermic heat of reaction must be provided at quite high temperatures with very intense heat fluxes. Although the direct fired furnaces used for this are quite efficient (> 90%), they are quite expensive including the cost of heat recovery systems. A plasma discharge reactor system uses electricity to drive the reaction and can be assumed to have an efficiency no greater than that of the power generation system (~60% for modern combined cycle combustion turbine plants). However, for the low temperature plasma, little energy is expended in gas heating and heat recovery systems are not needed. Thus, for the plasma system, somewhat higher energy consumption maybe be offset by simple process operation and lower cost for investment. This could be true especially for relatively small scale plants, where fuel gas is inexpensive, or where excess (off peak) power generation is available.

Conclusions

Carbon dioxide combined with steam reforming at moderate conversion levels has been demonstrated at near ambient conditions with moderate power consumption. Under most conditions, carbon formation was not an operational problem. If long term operation with high conversions can be demonstrated, a process can be envisaged wherein the cost and efficiency of using electricity to drive the reaction is counter-balanced by lower costs and simpler operation (without oxygen). For smaller resources and more remote locations, these tradeoffs may be highly advantageous. Whether there is a net reduction in carbon dioxide impact compared to more conventional reforming/partial oxidation synthesis gas generation processes can only be determined by a detailed life cycle analysis and not simply by the apparent reaction stoichiometry.

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