

# Combined Steam Reforming and Partial Oxidation of Methane to Synthesis Gas under Electrical Discharge

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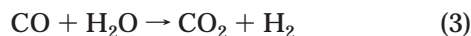
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An experimental study of synthesis gas production from simultaneous steam reforming and partial oxidation of methane using an ac corona discharge was conducted. The benefits of the combination of the two reactions reduce the pure oxygen requirement in the system and increase the thermal efficiency by transferring heat between the exothermic and endothermic reactions. The results show that the addition of water vapor greatly enhanced the conversions of methane and oxygen and improved the energy efficiency in an oxygen-lean system. The energy consumed to convert a methane molecule decreased dramatically from 68 to 13 eV/m<sub>c</sub> with an increase in the percentage of water vapor from 0 to 50% at a CH<sub>4</sub>/O<sub>2</sub> ratio of 5. At the conditions studied, input power had more influence on the methane and oxygen conversions than applied frequency.

## Introduction

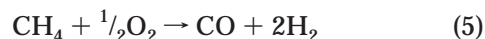
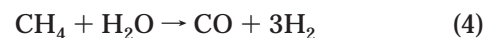
Synthesis gas, consisting of hydrogen and carbon monoxide, is an important raw material in chemical manufacture such as, Fischer–Tropsch synthesis to produce higher hydrocarbons (reaction 1), methanol synthesis (reaction 2), and hydrogen synthesis.<sup>1</sup> Additional hydrogen can be produced from synthesis gas by transformation of carbon monoxide in the water gas shift reaction (reaction 3) followed by carbon dioxide removal.<sup>2</sup>



The primary method of synthesis gas production has been steam reforming, shown in reaction 4. It is very useful to use low-cost materials to produce synthesis gas, and most existing synthesis gas plants use a steam and natural gas mixture via the steam reforming reaction over a Ni catalyst at high temperatures (>900 °C). The catalyst is placed in alloy tubes arranged inside a furnace with the heat of the highly endothermic reaction supplied by burners.<sup>2</sup> Expensive alloys are needed to tolerate the extremely high thermal fluxes through the tube walls<sup>3</sup> and to reduce potential issues of metal dusting caused by carbon monoxide production.<sup>4</sup> Though much energy can be recovered, it is as lower quality heat. The tendency for carbon deposition on the catalyst can also be one of its drawbacks. Consequently, steam reactors are usually operated with

a higher H<sub>2</sub>O/CH<sub>4</sub> ratio than the stoichiometric value. This results in higher H<sub>2</sub>/CO ratios (in the range of 3.4–5.0) than those required for Fischer–Tropsch synthesis and methanol production, and the high ratio of H<sub>2</sub>/CO also would limit the carbon chain growth in Fischer–Tropsch synthesis.<sup>5,6</sup> The H<sub>2</sub>/CO ratio that is obtained from steam reforming must be adjusted by the reverse water gas shift reaction or the purging of hydrogen for use as a supplemental fuel or downstream reactant.<sup>6</sup>

Partial oxidation of methane is another way to produce synthesis gas and gives a H<sub>2</sub>/CO ratio of 2 as shown in reaction 5. Noncatalytic partial oxidation of methane occurs only at very high temperatures. Much research has been focused on the partial oxidation of methane over different catalysts.<sup>7–12</sup> Although several catalysts are active for this reaction, a significant problem is rapid deactivation. Undesirable carbon formation cannot be avoided by increasing the O<sub>2</sub>/CH<sub>4</sub> ratio as well as the operating temperature, leading to potential explosion hazards, separation problems, gas-phase reactions, and a decrease in the synthesis gas selectivity.<sup>5</sup> Though the need of using pure oxygen as the feed gas has high investment and operating cost, this appears to be favored for several new commercial Fischer–Tropsch process designs.



A combination of noncatalytic partial oxidation and steam reforming has a benefit in terms of balancing the heat load. Methane conversions can be achieved up to 90% with residence times of up to 0.1 s. However, a typical steam reforming with oxygen reactor operates at about 2200 K in the combustion zone and 1200–1400 K in the catalytic zone.<sup>13</sup> Many researchers have studied steam reforming with oxygen to improve its efficiency. A possible improvement of this reaction is operation under a low-temperature plasma environment.

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## B

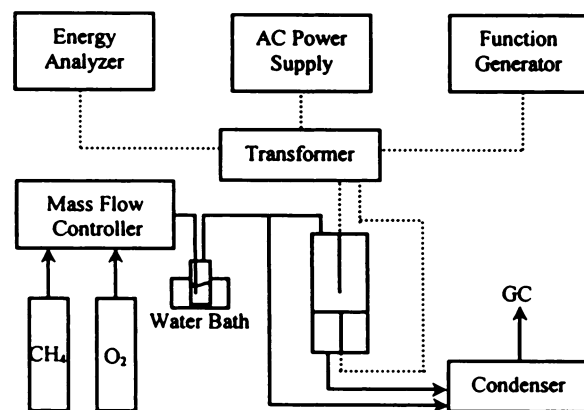
The use of plasma chemistry based technologies started as high-temperature equilibrium plasma processes for production of carbon black, acetylene, and hydrogen, but power costs are quite high. It was found that a low-temperature, nonequilibrium, plasma has benefits for some technologies because of its nonequilibrium properties.<sup>14</sup> The unique characteristic of the nonequilibrium plasma is that its electrons reach high temperatures of 10 000–100 000 K (1–10 eV), while the bulk gas temperature remains close to ambient temperature. Consequently, the low gas temperature of the plasma, while achieving high feed conversions, can allow selectivity control for the desired products<sup>14</sup> as well as result in lower power consumption and much less need for waste heat recovery.

A nonequilibrium discharge is an effective tool to generate energetic electrons, which can initiate a series of plasma chemical reactions such as ionization, dissociation, and excitation. Utilization of nonequilibrium plasmas as a “catalytic initiator” offers several potential advantages for chemical synthesis processes such as low cost, high selectivity, and fewer pollutants compared with other processes. It is a high productivity volumetric process; e.g., the interaction between accelerated charged particles (i.e., electrons and ions) and other chemical species (i.e., molecules and radicals) takes place in the whole plasma volume to promote the reaction, which is not possible in surface catalytic technologies.<sup>15</sup> Using electric discharges not only may provide heat to the reaction but also can initiate species in the homogeneous phase to speed up elementary reactions.<sup>2</sup> Nonequilibrium plasmas have been extensively studied as a possible way to initiate the reaction of methane to form various products for industrial application because of their effectiveness in the activation of methane at low gas temperatures and atmospheric pressure.<sup>16–21</sup> It is also of interest to find ways to improve synthesis gas production from methane by using electric discharges.<sup>2,22</sup> Also, it has been found that the energy consumption in this system is in the same range as net energy consumption for Fischer–Tropsch synthesis (~320 kW·h/1000 scf), and a simpler process may result. Applications for corona discharge processes have existed for over 100 years. The corona discharge plays an important role in several industrial applications such as electrostatic precipitation, electrophotography, static control in semiconductor manufacture, ionization instrumentation, generation of ozone, and destruction of toxic compounds. Some of these applications were reviewed by Chang et al.<sup>23</sup>

In this paper, a combination of steam reforming and partial oxidation of methane to synthesis gas under corona discharge has been studied to investigate the operational parameters, i.e., feed gas composition, residence time, applied frequency, and input power, affecting methane conversion, product distribution, and energy consumption.

### Experimental Section

The corona discharge was created in a reactor that consisted of a quartz tube with an inside diameter of 7.0 mm. The schematic diagram of the system is shown in Figure 1. The plasma was formed in the gap between two stainless steel electrodes that had a gap distance between them of 10 mm. The lower electrode was a circular plate, which was mounted perpendicular to the tube axis with holes in it to allow gas to pass through



**Figure 1.** Schematic diagram of the corona discharge reactor.

the reactor. The upper electrode was a wire suspended and centered axially within the reactor tube. All of the experiments were conducted at atmospheric pressure. The flow rates of feed gases were regulated by mass flow controllers (Porter Instrument Co. model 201). Water vapor was introduced into the reactor by passing the feed mixture of methane and oxygen through a bubbler in which the temperature was controlled to adjust the concentration of water vapor in the feed gas mixture. The average water mole fraction was confirmed by measuring the mass of water vaporized during the experiment. The feed gases were well mixed and then flowed downward through the reactor. The temperatures of the reactor and gas lines were maintained at 100 °C to avoid condensation of water vapor. The exhaust gas from the reactor was introduced into a condenser cooled by a mixture of dry ice and acetone to remove water and liquid organic products. However, liquid organic products were not found when analyzed with a Varian 3300 gas chromatograph (GC) with a Porapak Q column. The compositions of the feed gas mixture and the outlet gas were quantitatively measured by an online GC (HP 5890) with a thermal conductivity detector. The flow rates of the outlet gas were also measured by using a soap bubble flowmeter.

The ac power source consisted of an ac power supply, multifunction generator, and transformer. The domestic ac input of 120 V and 60 Hz was supplied through an Elgar ac power supply. A multifunction generator was used in conjunction with the power supply to form a sinusoidal waveform at the desired frequency. The output of the power supply was transmitted to a high-voltage (HVAC) transformer for stepping up the low-side voltage to the high-side voltage by a nominal factor of 125 at 60 Hz and then supplied to the reactor. An Exttech power analyzer was used to measure the power, power factor, current, frequency, and voltage at the low voltage side of the power circuit.

For this system, the conversions were defined as

$$\text{conversion of methane} = \frac{\text{(moles of CH}_4 \text{ consumed/moles of CH}_4 \text{ introduced)} \times 100\%}{100\%}$$

$$\text{conversion of oxygen} = \frac{\text{(moles of O}_2 \text{ consumed/moles of O}_2 \text{ introduced)} \times 100\%}{100\%}$$

The computation of selectivities was based on carbon converted as

$$\% \text{ product selectivity} = \frac{\text{total number of moles of carbon formed}}{\text{total number of moles of carbon reacted}} \times 100\%$$

$$\text{H}_2/\text{CO mole ratio} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}}$$

$$\text{CO/C}_2 \text{ mole ratio} = \frac{\text{moles of CO produced}}{\text{moles of ethane, ethylene, and acetylene produced}}$$

The total carbon selectivity of products containing a carbon atom was typically about 90%. However, no deposition of carbonaceous solid was observed inside the reactor throughout all experiments for the conditions studied. The “loss” of carbon probably resulted from experimental error. The residence time was calculated based on the volume of the reactor between the two electrodes. The energy consumed to convert a methane molecule (eV/m<sub>c</sub>) was calculated using input energy in terms of electronvolts (eV) per converted methane molecule and included power losses from all of the power equipment. For reference, 1 eV/m<sub>c</sub> amounts to about 31 kW·h/1000 scf of methane.

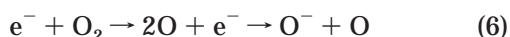
A standard experiment for this study encompasses the following conditions, from which parameter variations were made as discussed in the various results sections. The reactor had a gap width and residence time of 10 mm and 0.23 s, respectively, at a constant input power and applied frequency of 11 W and 300 Hz, respectively. The CH<sub>4</sub>/O<sub>2</sub> ratio was kept constant at 5 while 30% water vapor was added into the feed gas. The experiment could be reproduced with results within 7%.

## Results and Discussion

**Effect of the Feed Gas Composition.** The first experiments were performed to investigate the effect of the feed gas composition. Three CH<sub>4</sub>/O<sub>2</sub> ratios of 2, 3, and 5 were used with varying water-vapor contents of 0, 10, 30, and 50% of the total feed gas flow rate. The results, shown in Table 1, indicate that the feed gas composition is a significant parameter affecting both conversions and product distribution. Increasing the CH<sub>4</sub>/O<sub>2</sub> ratio leads to rapid decreases in both methane and oxygen conversions resulting from the reduction of oxygen availability in the system due to oxygen’s importance in methane activation. Similar results in both dielectric barrier discharges and corona discharges have been reported.<sup>16,18,24,25</sup>

Pure methane cannot be easily activated in the corona discharge because the ionization potentials of methane are greater than 12 eV,<sup>26</sup> higher than the average electron energy produced from the corona discharge used here. Because of its electronegative nature, oxygen relatively easily forms negative ions in the discharge. A number of possible pathways to activate oxygen molecules are shown in the following reactions:<sup>24</sup>

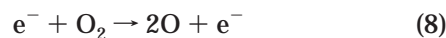
Dissociative attachment:



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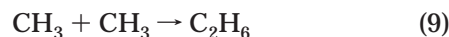


Dissociation:



The electrons produced in a corona discharge, with an average electron energy of about 5 eV, are sufficient to activate oxygen molecules by dissociative attachment, which requires the least energy in comparison with the other reactions.<sup>27,28</sup>

In this corona discharge, CH<sub>4</sub> is evidently activated by hydrogen abstraction to form CH<sub>3</sub>, CH<sub>2</sub>, CH, and C consecutively by active oxygen species, leading to a significant rate of methane conversion in the corona discharge. These CH<sub>3</sub>, CH<sub>2</sub>, and CH may couple to form ethane, ethylene, and acetylene, respectively (reactions 9–11, noting in addition that there is coupling to form radicals that can decompose to form the stable species containing less hydrogen, e.g., CH<sub>2</sub> + CH<sub>3</sub> → C<sub>2</sub>H<sub>5</sub> → C<sub>2</sub>H<sub>4</sub> + H). Additionally, ethane can be dehydrogenated to form ethylene, and ethylene is then dehydrogenated to form acetylene (overall reactions 12 and 13). Hydrogen may form predominantly via hydrogen abstraction by H. The maximum ethane selectivity was found at a CH<sub>4</sub>/O<sub>2</sub> ratio of 5, while the maximum carbon monoxide was found at a CH<sub>4</sub>/O<sub>2</sub> ratio of 2. The oxidation of methane to carbon oxides and water is more favored at higher oxygen concentrations. A higher CH<sub>4</sub>/O<sub>2</sub> ratio, with less oxygen, increases the probability of an activated C<sub>1</sub> species to react with another containing carbon to produce C<sub>2</sub> species and decreases the probability of an activated C<sub>1</sub> or C<sub>2</sub> species to react with active oxygen species, resulting in decreased production of other CH<sub>x</sub> species and carbon oxides. For this reason, ethane selectivity increases and the CO/C<sub>2</sub> ratio decreases with increasing CH<sub>4</sub>/O<sub>2</sub> ratio.



At a CH<sub>4</sub>/O<sub>2</sub> ratio of 2, adding water vapor to the feed gas had a negative effect on the conversions of methane and oxygen. The methane and oxygen conversions dramatically decreased while the product selectivities were not changed significantly with increasing water-vapor content. However, adding water vapor to the feed at higher CH<sub>4</sub>/O<sub>2</sub> ratios gave different results. At CH<sub>4</sub>/O<sub>2</sub> ratios of 3 and 5, a positive effect on the conversions of both methane and oxygen when adding water vapor was observed. Ethane selectivity decreased while carbon monoxide selectivity increased with increasing water content in an oxygen-lean system. It can be concluded that increasing the water content at constant high CH<sub>4</sub>/O<sub>2</sub> ratios of 3 and 5 shows a similar trend for conversions and selectivities as decreasing the CH<sub>4</sub>/O<sub>2</sub> ratio at constant water content. The conversions and product distribution depended more on the water-vapor content at the CH<sub>4</sub>/O<sub>2</sub> ratio of 5 than at the CH<sub>4</sub>/O<sub>2</sub> ratio of 3.

The main effect of the water content in this plasma system is to change the distribution of active species and therefore pathways. Water plays an important role in supplying active species, i.e., OH, H, and O, from its



D

**Table 1. Effect of the Feed Gas Composition on Conversions and Product Distribution (Gap Width, 10 mm; Residence Time, 0.23 s; Input Power, 11 W; Applied Frequency, 300 Hz)**

CH <sub>4</sub> /O <sub>2</sub> ratio	water (%)	conversion (%)		selectivity (%)						
		CH <sub>4</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> /CO	CO/C <sub>2</sub>
2	0	49	83	62	10	13	11	3	1.6	4.6
	10	46	86	57	8	16	11	3	1.7	3.8
	30	51	77	59	8	17	9	3	1.9	4.1
	50	40	57	62	8	16	10	3	2.0	4.3
3	0	19	40	47	10	8	20	11	2.2	2.4
	10	22	45	48	9	10	21	11	2.2	2.3
	30	30	52	47	5	18	15	6	2.5	2.4
	50	36	62	57	6	23	13	5	2.7	2.8
5	0	4	9	13	10	0	14	45	4.2	0.6
	10	8	13	23	4	6	19	25	3.6	0.9
	30	18	33	33	3	23	19	11	4.0	1.2
	50	30	55	39	3	28	13	5	3.8	1.7

dissociation reactions with relatively low electron energy within the plasma as shown in reactions 14 and 15.<sup>29</sup> These active species can activate methane to form other products by increasing the rate of formation of methyl radicals (reactions 16–18). Consequently, methane conversion increases with increasing water content. At a CH<sub>4</sub>/O<sub>2</sub> ratio of 2, oxygen species are relatively plentiful in the reactor. Adding active species to the system, which has enough active oxygen species, is not an effective way to enhance the methane conversion because of the dilution of methane. In addition, the product pathways do not change substantially with increased active species in the system because the system already has relatively abundant oxygen. The previous mention about the effect of the CH<sub>4</sub>/O<sub>2</sub> feed mole ratio on reaction pathways is also consistent with the effect of the water content on the selectivity because dissociation of water also gives active oxygen species. For CH<sub>4</sub>/O<sub>2</sub> ratios of 3 and 5, the selectivities of carbon monoxide and acetylene and the CO/C<sub>2</sub> ratio increase, but ethane, ethylene, and carbon dioxide selectivities decrease. These results suggest that active species from dissociation of water enhance secondary reactions of dehydrogenation and oxidation. The experiments also showed that the product distribution was slightly dependent on the water-vapor content but strongly dependent on the CH<sub>4</sub>/O<sub>2</sub> ratio. Thus, a change of the CH<sub>4</sub>/O<sub>2</sub> ratio more strongly affects the oxygen active species in the system than a change in the water content.

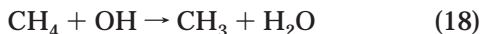
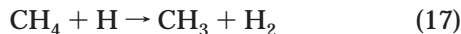
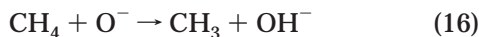
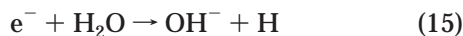
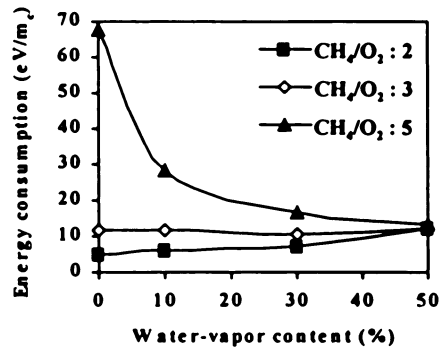


Figure 2 shows the effect of the feed gas composition on energy consumed to convert a methane molecule. Decreasing the CH<sub>4</sub>/O<sub>2</sub> ratio decreased the energy consumed to convert a methane molecule without significantly changing the electrical properties. This indicates that active oxygen species enhance the energy efficiency of the system by their facilitation of methane conversion and decreasing the energy consumed in converting a methane molecule. At a CH<sub>4</sub>/O<sub>2</sub> ratio of 5, the energy consumed to convert a methane molecule decreased dramatically from 68 to 13 eV/m<sub>c</sub> with an



**Figure 2.** Effect of the feed gas composition on energy consumed to convert a methane molecule: gap width, 10 mm; residence time, 0.23 s; input power, 11 W; applied frequency, 300 Hz.

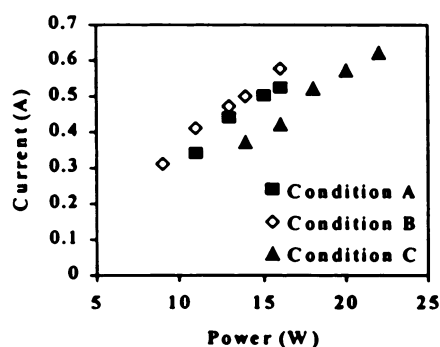
increase in the percentage of water vapor from 0 to 50, indicating that significant active oxygen species may be generated from water. However, the energy consumed to convert a methane molecule is constant with increasing water vapor at a CH<sub>4</sub>/O<sub>2</sub> ratio of 3. For a CH<sub>4</sub>/O<sub>2</sub> ratio of 2, adding water vapor not only reduced methane conversion but also reduced the energy efficiency slightly. It can be concluded that active species from dissociation of both oxygen and water remarkably enhance the energy efficiency of the system. However, high fractions of these oxygen-containing species increase the energy consumed to convert a methane molecule because some of them absorb energy without collision with methane molecules and the lower throughput of methane. It is possible to control the composition of synthesis gas and optimize the efficiency of the system by adjusting the feed gas composition.

**Effect of the Applied Power.** Table 2 shows the effect of the applied power in the ac corona discharge on methane reforming with oxygen and water vapor. The experiments were performed at three conditions with the same water vapor content of 30%. The first condition, condition A, was at a residence time of 0.23 s, a CH<sub>4</sub>/O<sub>2</sub> ratio of 5, and a frequency of 300 Hz. The second condition, condition B, was operated at the same condition as condition A except for a CH<sub>4</sub>/O<sub>2</sub> ratio of 3. The last condition, condition C, was performed at a residence time, frequency, and CH<sub>4</sub>/O<sub>2</sub> ratio of 0.06 s, 400 Hz, and 5, respectively. The power was increased from the lowest power that the discharge could sustain to the highest power that could be operated without carbon formation. Conditions A and B were operated at nearly the same power range. Condition C was operated at a higher power to increase conversion because the residence time was shorter. The relation between the input power and residence time will be

**Table 2.** Effect of the Power on Conversions and Product Distribution (Gap Width, 10 mm; Percentage of Water Vapor, 30%)

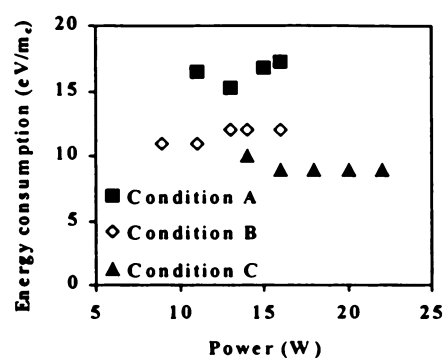
condition	power (W)	conversion (%)		selectivity (%)						
		CH <sub>4</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> /CO	CO/C <sub>2</sub>
A <sup>a</sup>	11	18	33	33	3	23	19	11	4.0	1.2
	13	22	49	35	4	17	19	9	3.5	1.5
	15	24	56	37	6	18	19	9	3.4	1.6
	16	24	59	35	6	18	18	8	3.6	1.6
B <sup>b</sup>	9	24	31	40	3	18	16	9	2.8	1.9
	11	30	52	47	5	18	15	6	2.5	2.4
	13	33	60	51	6	18	15	6	2.4	2.7
	14	34	65	50	7	18	14	5	2.5	2.7
	16	38	72	49	9	18	12	4	2.5	2.8
C <sup>c</sup>	14	9	7	32	2	40	11	6	5.0	1.1
	16	11	14	33	2	38	11	6	4.9	1.2
	18	13	20	33	3	38	12	6	4.8	1.2
	20	14	18	32	4	37	11	6	4.9	1.2
	22	16	16	30	4	37	11	6	4.7	1.2

<sup>a</sup> Condition A: CH<sub>4</sub>/O<sub>2</sub> ratio, 5; applied frequency, 300 Hz; residence time, 0.23 s. <sup>b</sup> Condition B: CH<sub>4</sub>/O<sub>2</sub> ratio, 3; applied frequency, 300 Hz; residence time, 0.23 s. <sup>c</sup> Condition C: CH<sub>4</sub>/O<sub>2</sub> ratio, 5; applied frequency, 400 Hz; residence time, 0.06 s.

**Figure 3.** Effect of the power on current (conditions are the same as those in Table 2).

discussed more clearly in the section on the effect of the residence time.

It was found experimentally that methane and oxygen conversions increased with the applied power at all conditions. The energies of individual electrons produced in the reactor are not the same but have a distribution. Only sufficiently high energy electrons can activate a particular molecule to form a *reactive* active species.<sup>20</sup> For the same reactor geometry, pressure, and gas, increasing the power increases the number of electrons at each energy level within the same distribution. An increase in the current, or the number of electrons over time, with increasing power, shown in Figure 3, also confirms this explanation. In other words, the density of the electrons with sufficient energy to activate molecules in the reactor increases with increasing power, resulting in increasing methane and oxygen conversions. For condition B, performed with higher oxygen content in the feed stream, increasing methane and oxygen conversions were higher than those in conditions A and C when the power was increased. In the system with higher oxygen partial pressure, oxygen has a greater probability of colliding with electrons to form active oxygen species and these active species may further activate methane molecules. At higher power, methane has a greater probability of being activated to form CH<sub>2</sub> and CH than CH<sub>3</sub>. Furthermore, CH<sub>2</sub> and CH are more reactive than CH<sub>3</sub> in the presence of oxygen, and the main products would be carbon oxides and/or ethylene and acetylene.<sup>21</sup> Acetylene can be formed directly from CH<sub>2</sub> and CH or from dehydrogenation of ethane and ethylene because the system has sufficiently high energy electrons and reactive H atoms to dehy-

**Figure 4.** Effect of the power on energy consumed to convert a methane molecule (conditions are the same as those in Table 2).

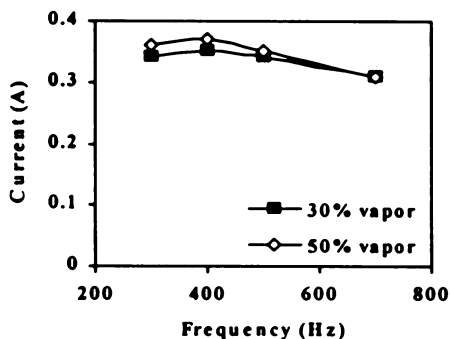
drogenate ethane to produce ethylene and then acetylene. The C<sub>2</sub> series can undergo further oxidation to carbon monoxide and carbon dioxide. As can be seen in Table 2, for conditions A and B, the CO/C<sub>2</sub> product ratio increases with increasing power. This shows that the secondary reaction of oxidation increases with increasing power. The selectivity change of condition B is larger than that of condition A. An explanation is that for condition B the oxygen conversion increase is higher than the methane conversion increase with increasing power, resulting in a shift in the balance between reaction pathways. However, for condition C, product selectivities are nearly constant, resulting in a constant CO/C<sub>2</sub> at about 1.2. Because condition C was operated at a short residence time, the primary products have less time to react with active species to undergo secondary reactions. The results from this study suggest that, under conditions with a sufficient source of activated oxygen, the secondary reactions of dehydrogenation and oxidation become predominant with increasing power.

The energy consumed to convert a methane molecule is relatively constant with increasing power, as shown in Figure 4. This indicates that the methane conversion increases linearly with increasing power in this conversion range. For all three conditions, A–C, the optimal input power is the highest power that can be operated without carbon formation. At the optimal input power, the maximum methane conversion is reached with the same energy efficiency as that at other input power.

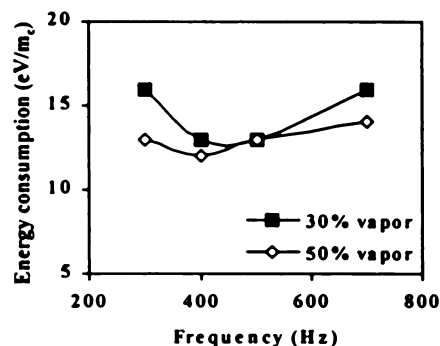
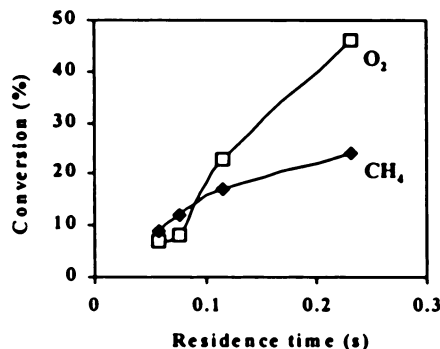
**Effect of the Frequency.** The results of methane reforming with oxygen and water vapor at different applied frequencies are shown in Table 3. The percentage of water vapor in the feed mixture was at 50 or 30%,

**Table 3. Effect of the Frequency on Conversions and Product Distribution (Gap Width, 10 mm; Residence Time, 0.23 s; CH<sub>4</sub>/O<sub>2</sub> Ratio, 5; Input Power, 11 W)**

water (%)	frequency (Hz)	conversion (%)		selectivity (%)						
		CH <sub>4</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> /CO	CO/C <sub>2</sub>
30	300	18	33	33	3	23	19	11	4.0	1.2
	400	22	38	33	3	25	18	9	4.0	1.3
	500	21	40	32	3	25	19	10	4.2	1.2
	700	18	27	34	2	31	18	11	4.5	1.2
50	300	30	55	39	3	28	13	5	3.8	1.7
	400	35	55	39	3	28	12	5	3.8	1.7
	500	30	51	40	3	29	12	6	3.8	1.7
	700	29	40	37	2	27	11	6	3.9	1.6

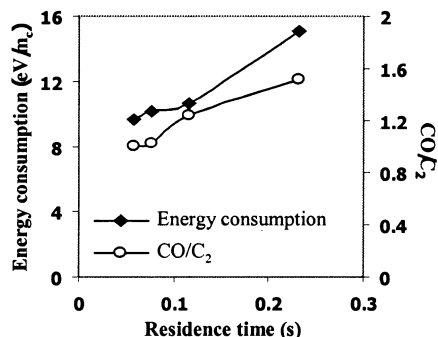
**Figure 5.** Effect of the frequency on current (conditions are the same as those in Table 3).

while the methane-to-oxygen ratio was kept constant at 5. The methane and oxygen conversions exhibited a maximum at a frequency of around 400 Hz. As the ac discharge is applied, the streamer corona discharge is thought to be a temporary dc corona discharge, with each electrode performing alternately as an anode or cathode.<sup>24</sup> The alternation of the electric field probably reduces and inhibits the accumulation of contaminants on the electrode surface as well as on the quartz tube wall.<sup>24</sup> The highest currents, of 0.35 and 0.37 A at 30% and 50% water vapor in the feed gas, respectively, are found at a frequency of 400 Hz, as shown in Figure 5. At the highest current, there were the largest numbers of electrons available to activate methane to produce all products, resulting in maximum methane and oxygen conversions. Beyond 400 Hz, the current decreases with increasing frequency. At 300 Hz, the current was slightly lower than the current at 400 Hz. The discharge turned to an arc discharge, and carbon was observed in the reactor when the frequency was decreased lower than 300 Hz. The reaction has to be operated at *carbon-free* conditions to have a significant reactive volume. Because this carbon is electrically conductive, the current tends to flow almost entirely through these carbon deposits. This reduces the number of discharge streamers and limits the number of energetic electrons that can interact with the feed gases in the reaction zone, resulting in a reduction of methane conversion as well as the reaction rate. Decreases in both current and conversions of methane and oxygen when the frequency was decreased from 400 to 300 Hz are probably due to the initiation of carbon formation in the reactor, resulting in a change in the plasma characteristics. The product distribution did not change significantly with changes in the frequency because methane and oxygen conversions change at the same rate with varying frequency. It can be concluded that decreasing the frequency increases methane conversion without a change of the reaction pathway. Figure 6 shows that the minimum energy consumed to convert a methane molecule was found at 400 Hz, the same frequency as

**Figure 6.** Effect of the frequency on energy consumed to convert a methane molecule (conditions are the same as those in Table 3).**Figure 7.** Effect of the residence time on conversion: gap width, 10 mm; CH<sub>4</sub>/O<sub>2</sub> ratio, 5; percentage of water vapor, 30%; input power, 14 W; applied frequency, 400 Hz.

that with maximum methane conversion. We may conclude that the optimum frequency for this system is about 400 Hz. For the conditions studied, the frequency had little influence on the methane conversion and energy consumed to convert a methane molecule in comparison with input power.

**Effect of the Residence Time.** To investigate the effect of the residence time, the experiments were conducted using a CH<sub>4</sub>/O<sub>2</sub> ratio of 5 and a water-vapor content in the feed of 30%. The effects of the residence time on methane and oxygen conversions are shown in Figure 7. Oxygen conversion increased significantly while methane conversion slightly increased with increasing residence time. The gas residence time is related to the contact time. When the residence time increases, giving a longer contact time, the collisions of gaseous molecules with sufficient energy electrons increase, resulting in higher methane and oxygen conversions. In this study, the power to initiate the reaction increases with decreasing residence time. The difference between oxygen and methane conversions increases with increasing residence time. This result



**Figure 8.** Effect of the residence time on the CO/C<sub>2</sub> molar ratio and energy consumed to convert a methane molecule: gap width, 10 mm; CH<sub>4</sub>/O<sub>2</sub> ratio, 5; percentage of water vapor, 30%; input power, 14 W; applied frequency, 400 Hz.

implies that oxygen not only reacts with methane but also reacts with the primary products.

Figure 8 shows the effect of the residence time on the CO/C<sub>2</sub> molar ratio and energy consumed to convert a methane molecule. The CO/C<sub>2</sub> molar ratio and energy consumed to convert a methane molecule increase with increasing residence time. These results conform to the previous explanation that, at longer residence time, oxygen active species also react with primary products as well as methane. At a longer residence time, these C<sub>2</sub> hydrocarbons have enough time to react further with oxygen to form carbon oxides. For this reason, the CO/C<sub>2</sub> product ratio increases with increasing residence time. Moreover, some of the energy is consumed by secondary reactions so the apparent energy consumed to convert a methane molecule increases at longer residence times.

## Conclusions

Experiments on methane reforming with water vapor and oxygen were performed in an ac corona discharge reactor. Because water is a cheaper reactant and easy to handle, it would be useful to develop synthesis gas production using steam as a co-reactant in a low-temperature methane reforming process. From the results, it was found that the coupling of methane increased with increasing CH<sub>4</sub>/O<sub>2</sub> ratio but the oxidation of methane to carbon oxides and water was more favorable at higher oxygen concentrations. Adding water vapor in the feed stream greatly enhanced the conversions of methane and oxygen in an oxygen-lean system but reduced the conversion of methane in the oxygen-rich system. Moreover, the energy consumption for methane conversion could be substantially reduced by adding water vapor at a CH<sub>4</sub>/O<sub>2</sub> ratio of 5. The product distribution was strongly influenced by the feed gas concentrations rather than the input power and applied frequency. The methane and oxygen conversions and energy efficiency exhibited maximum values at a frequency of around 400 Hz, and low frequencies result in carbon formation and loss of stability of the plasma. At the conditions studied, the input power had more influence on the methane and oxygen conversions than the applied frequency. With varying residence time, the maximum energy consumed to convert a methane molecule was found at the longest residence time.

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