

Synthesis Gas Production from Partial Oxidation of Methane with Air in AC Electric Gas Discharge

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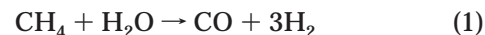
In this study, synthesis gas production in an AC electric gas discharge of methane and air mixtures at room temperature and ambient pressure was investigated. The objective of this work was to understand how the CH₄/O₂ feed mole ratio, ethane added, diluent gas, residence time, input power, applied frequency, and waveform, affected methane and oxygen conversions, product selectivities, and specific energy consumption. Methane and oxygen conversions increased with input power but decreased with increasing CH₄/O₂ feed mole ratio, flow rate, and gap distance. The experiments were performed at the frequency and power in the range of 200–700 Hz and 8–14 W, respectively, while the residence times were varied from 0.06 to 0.46 s. This study confirms that active oxygen is an important factor in enhancing methane conversion and energy efficiency in a discharge reactor. Ethane is the primary product that forms at short residence times and low energies. Methane conversion dropped dramatically but oxygen conversion increased with addition of ethane to the feed gas. Sinusoidal and square waveforms gave negligibly different results. Current was constant with varying CH₄/O₂ ratio and flow rate, but increased with increasing power and with decreasing gap distance and frequency. It was shown that the best condition was at 300 Hz and at the highest power used in each condition, since the maximum methane and oxygen conversions and synthesis gas selectivity as well as lowest specific energy consumption were found both with and without ethane in the feed gas. The minimum specific energy consumption, found at 300 Hz, were 21 and 14 eV/m_c for the CH₄/air system and the CH₄/air/C₂H₆ system, respectively. When studying the effect of residence time by varying the flow rate, the minimum energy consumption of 21 eV/m_c was found at 0.12 and 0.23 s. For any given input power or frequency, the CH₄/air system had a higher specific energy consumption than the CH₄/air/C₂H₆ system. Less energy was consumed to convert methane under the plasma environment with nitrogen as a diluent compared to helium, indicative of a third body effect.

Introduction

Natural gas, with methane as the main component, is an inexpensive, abundant, and low environmental impact resource. It is considered to be an increasingly important energy source and chemical feedstock in the 21st century. Intensive research efforts have been made to develop processes for converting methane into more valuable products. Although direct methane conversion to more valuable chemicals and liquid fuels is the most interesting,^{1–6} so far, no effective processes have been developed. Selective methane conversion to any particular products via synthesis gas is still being investi-

gated by a number of researchers.^{7,8} Synthesis gas plays an important role as a starting raw material in many kinds of chemical manufacture or liquid hydrocarbon production depending on the ratio of hydrogen to carbon monoxide.

Most synthesis gas is produced by the steam reforming reaction (reaction 1) in large furnaces to supply the necessary energy for this highly endothermic reaction.



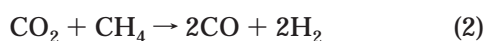
Industrially, steam reforming is performed over a Ni/Al₂O₃ catalyst.⁹ The typical problem is the tendency of carbon deposition on the catalyst. Consequently, steam reactors have to be operated with higher H₂O/CH₄ ratios

- (1) Fox, J. M. *Catal. Rev. Sci. Eng.* **1993**, *35*, 169.
- (2) Edwards, J. H.; Foster, N. R. *Fuel Sci. Technol. Int.* **1986**, *4*, 365.
- (3) Han, S.; Martenak, D. J.; Palermo, R. E.; Pearson, J. A.; Walsh, D. E. *J. Catal.* **1994**, *148*, 134.
- (4) Arutyunov, V. S.; Basevich, V. Ya.; Vedeneev, V. I. *Russ. Chem. Rev.* **1996**, *65*, 197.
- (5) Park, E. D.; Choi, S. H.; Lee, J. S. *J. Catal.* **2000**, *194*, 33.
- (6) Otsuka, K.; Wang, Y. *Appl. Catal. A* **2001**, *222*, 145.

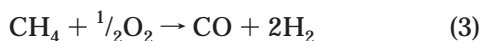
- (7) Otsuka, K.; Wang, Y.; Sunada, E.; Yamanaka, I. *J. Catal.* **1998**, *175*, 152.
- (8) Tsang, S. C.; Claridge, J. B.; Green, M. L. H. *Catal. Today* **1995**, *23*, 3.
- (9) Walker, A. V.; King, D. A. *J. Phys. Chem. B* **2000**, *104*, 6462.

than the stoichiometric value. This results in having higher H₂/CO ratios (in the range of 3.4–5.0) which is higher than the ratio required for methanol synthesis or Fischer–Tropsch process. To reduce the carbon deposition, not only is an excess of water needed but also a high temperature of about 1073 K must be used.⁸ For this reason, steam reforming requires a large amount of fuel and very high heat fluxes.

Carbon dioxide reforming with methane can also yield synthesis gas as shown in reaction 2. This reaction has been investigated by many researchers using various types of catalysts.^{10–13} Carbon dioxide reforming with methane has similar thermodynamics to the steam reforming process, which requires intensive energy input. The main difficulty of producing synthesis gas by carbon dioxide reforming with methane is coke formation, primarily due to the lower H/C ratio of this system, which deactivates the catalyst very quickly.



Partial oxidation of methane is another candidate process to produce synthesis gas as shown in reaction 3. A number of works have concentrated on the partial oxidation reaction at elevated pressures,^{14–17} and this is finding application in current GTL process designs. Using air instead of pure oxygen in the feed gas may reduce investment and operating cost but the dilution creates other problems as a trade off. Unfortunately, the main problem of partial oxidation is with methane combustion and its high temperatures, carbon deposition and the need to recover the excess energy.



Nonequilibrium plasmas have been widely studied for many applications such as ozone generation and destruction of NO_x, SO_x, H₂S, NH₃, and volatile organic compounds.^{18–23} A nonequilibrium discharge is an effective tool to generate energetic electrons, which can initiate a series of plasma chemical processes such as ionization, dissociation, and excitation. The generation and potential applications of plasmas have been reviewed comprehensively by Eliasson and Kogelschatz.^{18,24} Utilization of nonequilibrium plasmas as a catalyst may

reduce environmental problems in conjunction with having low cost, high selectivity, and energy-efficient syntheses. Moreover, the nonequilibrium plasma is a very effective process to promote chemical reactions due to the interaction between accelerated charged particles (i.e., electrons and ions) and other chemical species (i.e., molecules and radicals) taking place in the whole reactor volume, which is not possible in surface catalysis technologies.²⁵ Corona discharges are among the common methods for producing nonequilibrium plasmas at atmospheric pressure and room temperature. Because a corona discharge is easy to establish, it has a wide application in a variety of processes, including synthesis of chemicals.²⁶ A corona discharge has been studied for methane conversion both with and without catalyst.^{27–30}

The purpose of this work was to study the partial oxidation of methane in air under the discharge environment as a novel method to reduce the cost of synthesis gas production, which has a major impact on the overall economy of a plant, accounting for about 60% of the investment cost of methanol plants. CH₄/air feed mole ratio, residence time, input power, input frequency, and waveform were varied to determine the effects of these parameters on methane and oxygen conversions and product selectivities. In addition, the effect of ethane partial pressure on plasma reactions was investigated due to the significant amounts of ethane found within natural gas. Comparison between the use of nitrogen and helium as diluent gas was also investigated.

Experimental Section

The corona discharge was created in a reactor that was made of a quartz tube with an inside diameter of 7.0 mm. The schematic diagram of the system is shown in Figure 1. The lower electrode was a circular plate that was mounted perpendicular to the tube axis with holes in it to allow gas to pass through the reactor. The diameter of the circular plate was 6.0 mm. The upper electrode was a wire suspended and centered axially within the reactor tube. All the experiments were conducted at atmospheric pressure and room temperature. The flow rates of feed gases were regulated by a set of mass flow controllers (Porter Instrument Co., model 201). The feed gases were well mixed and then introduced downward through the reactor. The exhaust gas from the reactor flowed into a condenser cooled by a mixture of dry ice and acetone to remove water and other condensates. The feed mixture and exhaust gas that came out of the condenser were analyzed by an on-line gas chromatograph (HP5890) with a thermal conductivity detector (TCD). The exhaust gas was also tested by a NO analyzer (42 C NO–NO₂–NO_x, Thermo Environmental Instrument, Inc.) to determine NO_x formation as a result of using air, composed of about 79% nitrogen and 21% oxygen, through the plasma discharge. Interestingly, under the studied conditions, nitrogen oxides were not detected. Hence, it can be concluded that the formation of nitrogen oxides is generally

- (10) Wang, S.; Lu, G. Q. *Energy Fuels* **1996**, *10*, 896.
 (11) Zhang, Z.; Verykios, X. E.; MacDonald, S. M.; Affrossman, S. *J. Phys. Chem.* **1996**, *100*, 744.
 (12) Yan, Z.-F.; Ding, R.-G.; Song, L.-H.; Qian, L. *Energy Fuels* **1998**, *12*, 1114.
 (13) Wang, S.; Lu, G. Q. *Ind. Eng. Chem. Res.* **1999**, *38*, 2615.
 (14) Lott, J. L.; Sliepcevich, C. M. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 67.
 (15) Hardwicke, N. L.; Lott, J. L.; Sliepcevich, C. M. *Ind. Eng. Chem. Process Des. Dev.* **1969**, *8*, 133.
 (16) Feng, W.; Knopf, F. C.; Dooley, K. M. *Energy Fuels* **1994**, *8*, 815.
 (17) Vernon, P. D. F.; Green, M. L. H.; Cheetham, A. K.; Ashcroft, A. T. *Catal. Today* **1992**, *13*, 417.
 (18) Eliasson, B.; Kogelschatz, U. *IEEE Trans. Plasma Sci.* **1991**, *19*, 309.
 (19) Penetrante, B. M.; Hsiao, M. C.; Merritt, B. T.; Vogtlin, G. E.; Wallman, P. H. *IEEE Trans. Plasma Sci.* **1995**, *23*, 679.
 (20) Li, J.; Sun, W.; Pashaie, B.; Dhali, S. K. *IEEE Trans. Plasma Sci.* **1995**, *23*, 672.
 (21) Futamura, S.; Yamamoto, T. *IEEE Trans. Ind. Appl.* **1997**, *33*, 447.
 (22) Futamura, S.; Zhang, A.; Yamamoto, T. *IEEE Trans. Ind. Appl.* **2000**, *36*, 1507.
 (23) Futamura, S.; Einaga, H.; Zhang, A. *IEEE Trans. Ind. Appl.* **2001**, *37*, 978.

- (24) Eliasson, B.; Kogelschatz, U. *IEEE Trans. Plasma Sci.* **1991**, *19*, 1063.
 (25) Mutaf-Yardimci, O.; Saveliev, A. V.; Fridman, A. A.; Kennedy, L. A. *Int. J. Hydrogen Energy* **1998**, *23*, 1109.
 (26) Chang, J.-S.; Lawless, P. A.; Yamamoto, T. *IEEE Trans. Plasma Sci.* **1991**, *19*, 1152.
 (27) Liu, C.; Marafee, A.; Hill, B.; Xu, G.; Mallinson, R.; Lobban, L. *Ind. Eng. Chem. Res.* **1996**, *35*, 3295.
 (28) Marafee, A.; Liu, C.; Xu, G.; Mallinson, R.; Lobban, L. *Ind. Eng. Chem. Res.* **1997**, *36*, 632.
 (29) Liu, C.; Marafee, A.; Mallinson, R.; Lobban, L. *Appl. Catal. A* **1997**, *164*, 21.
 (30) Liu, C.; Mallinson, R.; Lobban, L. *J. Catal.* **1998**, *179*, 326.

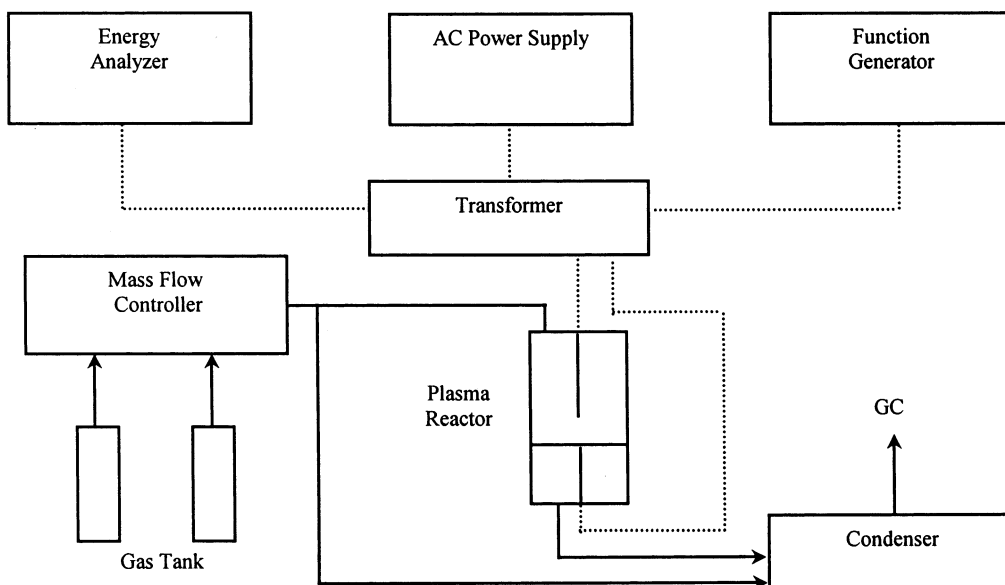


Figure 1. Schematic diagram of reactor system.

negligible in this plasma environment. The condensate product from the condenser was analyzed by Varian 3300 GC with a Porapak Q column. Liquid organic products were not found.

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 with a multifunction generator to generate the waveform and frequency. The variable output (0–120V AC) of this supply, from which power measurements are reported, was transmitted to a high voltage alternative current (HVAC) transformer for stepping up the low side voltage to the high side voltage by a nominal factor of 125 at 60 Hz. The electrodes were connected to the HVAC by stainless steel wires. The output obtained from the HVAC transformer was then supplied to the reactor. An Extech power analyzer was used to measure the power, power factor, current, frequency, and voltage at the low side voltage of the power circuit. For this study, the conversions are defined as

$$\text{conversion of methane} = \frac{\text{moles of CH}_4 \text{ consumed}}{\text{moles of CH}_4 \text{ introduced}} 100$$

$$\text{conversion of oxygen} = \frac{\text{moles of O}_2 \text{ consumed}}{\text{moles of O}_2 \text{ introduced}} 100$$

$$\text{conversion of ethane} = \frac{\text{moles of C}_2\text{H}_6 \text{ consumed}}{\text{moles of C}_2\text{H}_6 \text{ introduced}} 100$$

The selectivity computation of products containing carbon atom is based on carbon converted, while hydrogen selectivity is calculated based on hydrogen converted as

$$\text{Selectivity of product containing carbon atom} = \frac{\text{carbon molar flow rate of a product}}{\text{rate of carbon reacted}} 100$$

$$\text{H}_2 \text{ selectivity} = \frac{[(\text{H}_2 \text{ product molar flow rate})(2)]}{\text{rate of H reacted}} 100$$

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

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

Specific energy consumption (eV/m_c) is defined as energy

consumed in terms of electron-volt (eV) per molecule of converted hydrocarbon (1 eV/molecule = 96.48 kJ/mol = 0.033877 kWh/scf). Residence time is calculated from dividing the volume of the empty reactor between the two electrodes by the volumetric flow rate of feed gas.

The standard experiment consisted of a feed mixture of methane and air at a ratio of 3:4.8 corresponding to CH₄/O₂ ratio of 3:1. By keeping the total flow rate of feed gas and gap distance between the two electrodes constant at 100 cm³/min and 10 mm, respectively, the standard residence time was 0.23 s. All volumetric flow rates are based upon standard conditions. The input power and applied frequency were fixed for the standard experiment at 10 W and 300 Hz with a sinusoidal waveform.

Results and Discussion

Effect of CH₄/O₂ Feed Mole Ratio. To study the effect of CH₄/O₂ feed mole ratio, the CH₄/O₂ ratio in the feed gas was varied from 2:1 to 5:1. The results show that methane and oxygen conversions decreased significantly from 35 to 7% and from 50 to 11%, respectively, with increasing CH₄/O₂ ratio as shown in Figure 2a even though the nitrogen partial pressure decreased from 0.56 to 0.39 atm. It was found that for the pure methane system operated under the same conditions, a very low methane conversion (~3%) was observed. This result affirms the point that methane cannot be activated to a significant degree without oxygen under these conditions. It has also been reported that the presence of active oxygen species enhances the methane conversion in both a dielectric barrier discharge^{31,32} and corona discharge.^{27,30} The average electron energies produced from the corona discharge of about 5 eV²⁴ are sufficient to activate oxygen molecules into negatively charged oxygen ions but are not sufficient to ionize a methane molecule, having an ionization potential greater than 12 eV.³³ The negatively charged oxygen is thought

(31) Larkin, D. W.; Caldwell, T. A.; Lobban, L. L.; Mallinson, R. G. *Energy Fuels* **1998**, *12*, 740.

(32) Yao, S. L.; Takemoto, T.; Ouyang, F.; Nakayama, A.; Suzuki, E. *Energy Fuels* **2000**, *14*, 459.

(33) Sorensen, S. L.; Karawajczyk, A.; Stromholm, C.; Kirm, M. *Chem. Phys. Lett.* **1995**, *232*, 554.

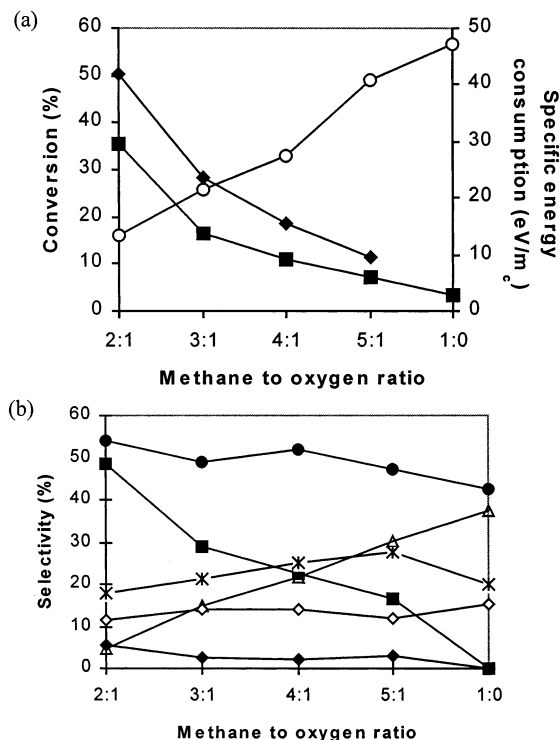


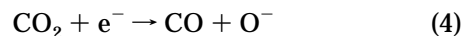
Figure 2. Effect of CH₄/O₂ ratio (a) on conversions of CH₄ (■) and O₂ (◆) and specific energy consumption (○); (b) on selectivities of CO (■), CO₂ (◆), H₂ (●), C₂H₆ (△), C₂H₄ (*), and C₂H₂ (◇). Overall flow rate, 100 cm³/min; gap distance, 10 mm; residence time, 0.23 s; input power, 10 W; and applied frequency, 300 Hz.

to activate a methane molecule by abstracting a hydrogen atom from the methane to form the methyl radical (CH₃) in the corona discharge. A higher CH₄/O₂ ratio decreases the probability of methane colliding with the active oxygen resulting in less chance of methane molecules being activated resulting in lower methane conversion. The specific energy consumption increases dramatically from 13 to 41 eV/m_c with increasing ratio of CH₄/O₂ in the feed from 2:1 to 5:1 as shown in Figure 2a. It can be concluded that active oxygen is a very important factor to enhance methane conversion and energy efficiency in the corona discharge reactor. The current is approximately constant at about 0.39 A for all ratios of CH₄/O₂. This implies that the electron flow between the two electrodes does not depend on the composition of the feed mixture over the range of this study. Also, at a constant gap, the breakdown voltage is only slightly dependent on the gas composition over this range. Therefore the distribution of electron energies is fairly constant.

Figure 2b shows the effect of CH₄/O₂ ratio on product selectivities. For the pure methane system, the major products were hydrogen and ethane. The C₂ selectivity was only 73% and the remaining fraction of converted carbon atoms from methane molecules was reacted to form carbon deposits in the reactor. With increasing CH₄/O₂ ratio from 2:1 to 5:1, the selectivity of hydrogen and acetylene were relatively constant around 50 and 13%, respectively, while carbon monoxide selectivity decreased significantly from 48 to 16%. The selectivity of ethane rapidly increased from 5 to 30%, while ethylene selectivity moderately increased from 18 to 28%. With increasing CH₄/O₂ ratio, the probability of

an activated methane species (such as methyl) reacting with another one resulting in dimerization is relatively more probable in comparison to the direct reaction with oxygen. Hence, the C₂ selectivity increased as oxygen is lowered in the gas feed. Caldwell et al. studied partial oxidation of methane with pure oxygen.³⁴ They varied CH₄/O₂ ratio from 2:1 to 19:1 at the same reactor configuration, residence time, gap distance, input power, and applied frequency as this work. They found that methane conversion increased from less than 2% at the lowest oxygen concentration to nearly 45% at the highest oxygen concentration. Carbon monoxide selectivity decreased rapidly from 55 to 19%, while ethane selectivity increased dramatically from under 4 to nearly 50%. The other products changed slightly. All product selectivities were very close to this work. Compared to partial oxidation of methane with pure oxygen, methane partial oxidation with air has a slightly lower methane conversion because methane and oxygen were diluted by nitrogen. The lower reactant concentration at a constant CH₄/O₂ ratio has no effect on product distribution.

At elevated temperatures, when oxygen is introduced into the reaction system, methane as well as C₂ products can be further oxidized into carbon monoxide as suggested by the increasing CO/C₂ ratio from 0 to 2.8 with decreasing CH₄/O₂ ratio from 1:0 to 2:1. Typically, heterogeneous catalytic oxidative coupling and partial oxidation of methane reactions can produce significant amounts of carbon dioxide due to homogeneous reactions at the high temperatures required. For these experiments, the carbon dioxide selectivity remained very low and almost constant throughout the range of oxygen partial pressures studied here. All other experiments revealed similar behavior. It can be explained that the dissociative attachment of carbon dioxide can occur within the electron energies of corona discharges to produce carbon monoxide and active oxygen (reaction 4),²⁷ therefore carbon dioxide production under electrical discharge is lower than for homogeneous partial oxidation.



Hydrogen radicals and hydrogen molecules can easily react with oxygen to form water and so hydrogen selectivity remained almost unchanged with decreasing CH₄/O₂ molar ratio. The H₂/CO molar ratio was found to be 2.2 at a CH₄/O₂ ratio of 2:1 conforming to the theoretical stoichiometric ratio for the partial oxidation of methane. When the CH₄/O₂ ratio was higher than 2:1, the H₂/CO molar ratio increased to 5.8:1 due to decreasing carbon monoxide production, releasing further hydrogen from carbon products.

Effect of Ethane Addition. The effect of ethane addition on methane conversion and product selectivities can be clearly seen in Tables 1 and 2. Ethane was added to the mixture of methane and air by keeping the ratio of CH₄/O₂/C₂H₆ at 2:1:1. For this reason, the results are compared with and without ethane in the feed gas at the same hydrocarbon to oxygen feed mole

(34) Caldwell, T. A.; Le, H.; Lobban, L. L.; Mallinson, R. G. In *Surface Science and Catalysis, Volume 136: Natural Gas Conversion VI*; Iglesia, E, et al., Eds.; Elsevier: New York, 2001; p 265.

Table 1. Effects of Power and Ethane Addition on Partial Oxidation Reaction of Methane; Overall Flow Rate, 100 cm³/min; Gap Distance, 10 mm; Residence Time, 0.23 s; and Applied Frequency, 300 Hz

CH ₄ :O ₂ :C ₂ H ₆ (molar ratio)	power (W)	conversion (%)				selectivity (%)					H ₂ /CO	CO/C ₂	current (A)	eV/m _c
		CH ₄	O ₂	C ₂ H ₆	H ₂	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆				
4:1:0	8	9	11		45	16	0	12	23	25	5.6	0.5	0.28	27
	9	10	16		47	18	0	12	23	26	5.2	0.6	0.33	29
	10	11	18		52	23	2	14	25	22	4.6	0.8	0.38	27
3:1:0	11	15	31		51	28	2	14	23	14	3.6	1.1	0.45	22
	8	12	14		47	23	0	12	22	22	4.0	0.8	0.29	25
	9	16	27		53	32	3	15	22	13	3.3	1.3	0.37	20
2:1:1	10	20	34		54	36	3	16	19	10	3.0	1.6	0.39	20
	11	26	46		59	40	3	18	17	7	2.9	1.9	0.42	17
	8	4	21	28	38	14	1	8	62	0	4.3	0.1	0.27	21
	9	6	35	42	45	17	1	11	57	0	4.0	0.2	0.32	16
	10	7	48	53	48	21	1	13	53	0	3.5	0.3	0.36	14

Table 2. Effect of Frequency and Ethane Addition on Partial Oxidation Reaction of Methane; Overall Flow Rate, 100 cm³/min; Gap Distance, 10 mm; Residence Time, 0.23 s; and Input Power, 10 W

CH ₄ :O ₂ :C ₂ H ₆ (molar ratio)	frequency (Hz)	conversion (%)				selectivity (%)					H ₂ /CO	CO/C ₂	current (A)	eV/m _c
		CH ₄	O ₂	C ₂ H ₆	H ₂	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆				
3:1:0	200	18	30		54	31	3	15	18	12	3.4	1.4	0.37	22
	300	19	31		55	33	3	14	19	10	3.3	1.5	0.39	21
	400	17	26		54	30	3	14	21	14	3.6	1.2	0.35	24
	500	15	20		54	28	2	13	23	18	3.8	1	0.32	27
	600	14	17		53	28	2	12	24	20	3.9	1	0.31	30
2:1:1	700	12	13		53	27	0	11	25	21	3.9	0.9	0.30	34
	300	7	48	53	48	21	1	13	53	0	3.5	0.3	0.36	14
	400	7	46	50	46	20	2	11	56	0	3.6	0.3	0.35	14
	500	5	35	40	41	17	1	10	59	0	3.9	0.2	0.32	18
	600	5	33	39	41	15	1	9	62	0	4.3	0.1	0.30	18
	700	5	29	37	38	14	1	8	63	0	4.3	0.1	0.29	19

ratio. Ethane conversion is higher than methane conversion by more than 5 times due to the fact that ethane has a lower net energy for hydrogen abstraction as the carbon–hydrogen bond dissociation energy in ethane is 410 kJ/mol, while the carbon–hydrogen bond dissociation energy in methane is 431 kJ/mol.³⁵ It can be concluded that ethane is easier to activate than methane. Methane conversion dropped more than 2 times but oxygen conversion increased when ethane was added into the feed gas. Ethane conversion was very high, up to 53% at an input power of 10 W and an applied frequency of 300 Hz. In contrast to this work, it was found that methane conversion increased when ethane was added in the feed gas at a high CH₄/C₂H₆ ratio in the feed gas without oxygen in a dielectric barrier discharge reactor.³⁶ The result can be explained that in the absence of oxygen, adding ethane enhances methane conversion because ethane is more easily activated in the reactor and these ethane-derived active species activate methane more easily than methane itself. In the presence of oxygen, ethane is easy to be activated and react with oxygen resulting in lower probability of methane being activated by oxygen. Carbon monoxide and hydrogen selectivities in the CH₄/air/C₂H₆ system were usually lower than in the CH₄/air system at the same power and frequency. A doubling of ethylene selectivity was found in the CH₄/air/C₂H₆ system as compared to the CH₄/air system. This further shows that ethylene is produced directly from the dehydrogenation reaction of ethane. The specific energy consumption in this case was calculated as power consumption per molecule of methane and ethane converted. The

energy efficiency increased with addition of ethane to the feed gas. Larkin and his group showed that the energy efficiency increased by 49% for the C₂H₆/O₂ ratio at 2:1, compared to CH₄/O₂ ratio at 2:1 in silent electric discharge reactor.³⁷

Effect of Diluent Gas. It has been found that addition of helium does not cause lower methane conversion due to the lower methane partial pressure but it enhances methane conversion^{36,38} as well as improves methanol production.³⁹ This experiment was performed in this study to compare the effect of nitrogen, the major component of air and helium on conversions and product selectivities as well as specific energy consumption. Helium and pure oxygen were introduced with methane as feed gases instead of using air by keeping the O₂/He ratio of 21:79. The CH₄/O₂/He system could be operated at higher power than the CH₄/air system. Power was varied from 8 to 14 W for the CH₄/O₂/He system at CH₄/O₂ ratio of 3:1 as shown in Table 3 but could be varied only 8–11 W for the CH₄/air system at the same CH₄/O₂ ratio as shown in Table 1. The lower limit to initiate the plasma depends on the breakdown voltage, while the upper limit of increasing power is limited by carbon formation. Both methane and oxygen conversions and current increased significantly with increasing power in both systems, but at different levels. The current in the CH₄/O₂/He system was higher than in the CH₄/air system but the conversions were lower. The specific energy consumption decreased from

(37) Larkin, D. W.; Lobban, L. L.; Mallinson, R. G. *Ind. Eng. Chem. Res.* **2001**, *40*, 1594.

(38) Larkin, D. W.; Leethochawalit, S.; Caldwell, T. A.; Lobban, L. L.; Mallinson, R. G. In *Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies*; Eliasson, B., Riemer, P., Wokaun, A., Eds.; Pergamon: Amsterdam, 1999; p 397.

(39) Okumoto, M.; Takashima, K.; Katsura, S.; Mizuno, A. *The Asia-Pacific Workshop on Water and Air Treatment by Advanced Oxidation Treatments*; 1998; p 106.

(35) Dean, J. A. *Lange's Handbook of Chemistry*; 15th ed.; McGraw-Hill: New York, 1999.

(36) Thanyachotpaiboon, K.; Chavadej, S.; Caldwell, T. A.; Lobban, L. L.; Mallinson, R. G. *AIChE J.* **1998**, *44*, 2252.

Table 3. Effects of Power and Waveform on Partial Oxidation Reaction of Methane with Oxygen in Helium; CH₄/O₂/He Molar Ratio, 3:1:3.8; Overall Flow Rate, 100 cm³/min; Gap Distance, 10 mm; Residence Time, 0.23 s; and Applied Frequency, 300 Hz

wave form	power (W)	conversion (%)				selectivity (%)							current	
		CH ₄	O ₂	C ₂ H ₆	H ₂	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	H ₂ /CO	CO/C ₂	(A)	eV/m _c
sinusoidal	8	8	16		31	23	3	0	12	39	2.8	1.3	0.39	35
	10	12	19		33	22	3	0	19	36	3.1	0.9	0.53	30
	12	15	23		38	24	3	0	24	32	3.2	0.8	0.65	30
	14	17	29		40	26	4	0	26	27	3.1	0.8	0.76	30
square	8	11	18		33	22	3	0	15	34	3.0	0.9	0.35	26
	10	11	17		33	24	3	0	17	37	2.8	0.9	0.48	35
	12	15	22		37	23	3	0	23	31	3.2	0.9	0.60	25
	14	18	28		39	25	3	0	25	26	3.2	1.0	0.69	29

25 to 17 eV/m_c for the CH₄/air system and from 35 to 30 eV/m_c for the CH₄/O₂/He system with increased power. The CH₄/air system required less energy to convert methane. The result shows that helium acts as an energy sink in the reactor. At the same input power, methane and oxygen conversions of the CH₄/O₂/He system were lower than of the CH₄/air system because more of supplied power was absorbed by helium. With less available power, acetylene was not produced in the CH₄/O₂/He system.

Effect of Residence Time. Residence time is one of the most important factors for chemical reaction processes. The effect of residence time on the discharge system was studied in two parts, changing residence time by varying flow rate and by varying gap distance. First, the flow rate was varied from 50 to 400 cm³/min corresponding to residence times ranging from 0.06 to 0.46 s. As can be seen in Figure 3a, both methane and oxygen conversions increase substantially from 3 to 25% and 0.4 to 45%, respectively with increasing residence

time. Compared to this work at the same CH₄/O₂ ratio and same conditions, partial oxidation of methane with pure oxygen has higher methane and oxygen conversions.³⁴ With increasing residence time, using methane and pure oxygen as a feed gas, from 0.06 to 0.46 s, methane conversion increased from 10% to 35% and oxygen conversion increased from 15% to 60%.³⁴

In these experiments, current was observed to be almost constant at 0.36 A for all residence times. When the residence time decreases, the contact time between methane and oxygen with electrons decreases resulting in decreasing conversions of both methane and oxygen. The minimum specific energy consumption was found at residence times ranging from 0.12 to 0.23 s as shown in Figure 3a. At a residence times lower than 0.12 s, specific energy consumption decreased with increasing residence time since electrons have enough time to release energy through inelastic collisions with oxygen and methane to produce the active species. At residence time higher than 0.23 s, specific energy consumption increased with increasing residence time because of lower probabilities of reacting with lower partial pressures of reactants and some of the power may be consumed by secondary reactions.

Figure 3b illustrates the effect of residence time by varying flow rate on product selectivities. The detectable products at a residence time of 0.06 s were only hydrogen and ethane; corresponding to a very low oxygen conversion. When the residence time increased to 0.08 s, ethylene was found and its selectivity was relatively constant at about 20% for all other residence times. With increasing residence time from 0.12 to 0.46 s, carbon monoxide selectivity increased from 18 to 40% and carbon dioxide selectivity increased slightly from 0 to 3%. Acetylene was found only at residence times of 0.23 and 0.46 s with a constant selectivity of 14%. Ethane selectivity decreased from 75 to 10%, while hydrogen selectivity increased from 36 to 55% with increasing residence time. The results imply that under the conditions studied, ethane is a primary synthesis product from the coupling reaction of methane via methyl radicals. At higher residence time, ethane is further decomposed by dehydrogenation to ethylene and then ethylene is dehydrogenated to form acetylene. The oxidation reaction of these hydrocarbons produces carbon oxides.

After investigating the effect of residence time by varying flow rate, the effect of residence time by varying gap distance was studied. The gap distance was increased from 8 to 14 mm while the flow rate was kept constant, and so the residence time was increased from 0.18 to 0.32 s. As can be see from Figure 4, both

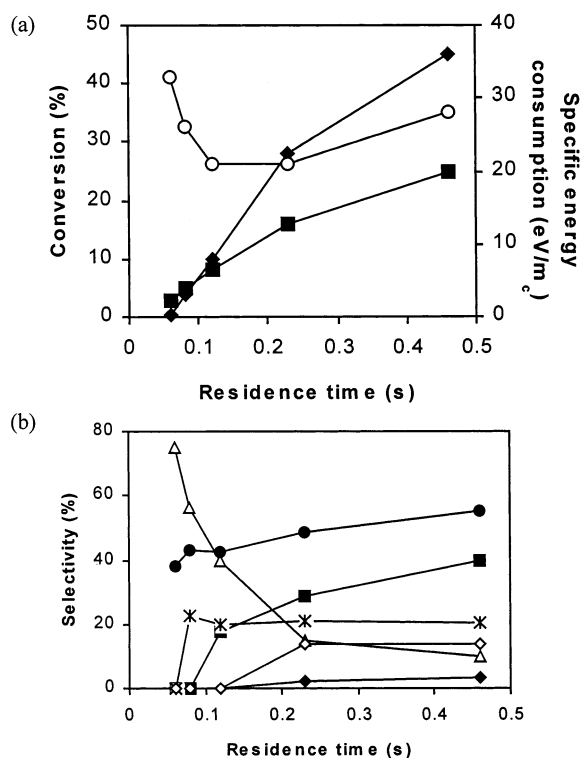


Figure 3. Effect of residence time by varying flow rate (a) on conversions of CH₄ (■) and O₂ (◆) and specific energy consumption (○); (b) on selectivities of CO (■), CO₂ (◆), H₂ (●), C₂H₆ (△), C₂H₄ (*), and C₂H₂ (◇). CH₄/O₂ molar ratio, 3:1; gap distance, 10 mm; input power, 10 W; and applied frequency, 300 Hz.

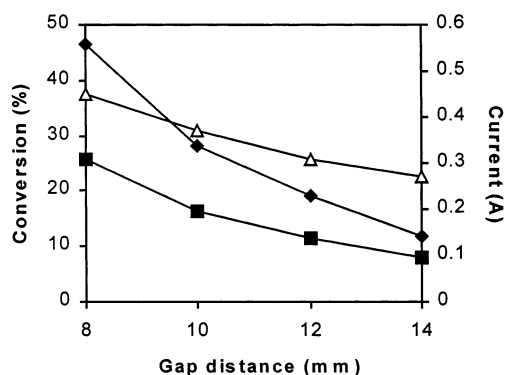


Figure 4. Effect of gap distance on conversions of CH₄ (■) and O₂ (◆), and current (△). CH₄/O₂ molar ratio, 3:1; overall flow rate, 100 cm³/min; input power, 10 W; and applied frequency, 300 Hz.

methane and oxygen conversions rapidly decrease from 26% to 8% and from 46% to 12%, respectively, with increasing gap distance. As discussed in the effect of residence time by varying flow rate, both conversions of methane and oxygen increase with increasing contact time in the reactor. It can be implied that there is another factor besides contact time affecting conversion when the gap distance is varied. The charge characteristics of the discharge change with varying gap distance. The breakdown voltage required for initiating the discharge and the lowest power supporting a discharge increase with increasing gap distance. The change in the electric field strength due to increased breakdown voltage of the gas gap results in a shift of the average electron energy to a lower value thereby reducing the number of electrons with energies capable of initiating reactions, so lower conversion is observed despite longer contact times. The effect of reducing the number of electrons and their energy with increasing gap distance is clearly shown in terms of current in Figure 4. Hence, this indicates that the effect of electric field strength dominates over the contact time effect on the conversions when varying the gap distance.

The present results of the effect of gap distance experiments do not agree with the previous experiments performed by Hill.⁴⁰ He showed that both conversions of methane and oxygen increased with increasing gap distance while the current decreased. The differences in the experimental results can be explained in that the present work was conducted at constant input power, while the previous one was done at constant voltage.

With increasing gap distance, the selectivities decreased from 57 to 41% for hydrogen, from 39 to 19% for carbon monoxide and from 3 to 0% for carbon dioxide and from 20 to 0% for acetylene while ethane selectivity increased from 7 to 30% and ethylene was almost constant about 20%. From these results it can be concluded that ethane is produced even at low currents and energies. However, the specific energy consumption increased dramatically from 14 to 45 eV/m_c with increasing gap distance. At higher electric field strength (smaller gaps), more electrons have sufficient energy to activate oxygen so the energy "efficiency" increases.

Effect of Input Power. The input power has been found to be a significant variable affecting the perfor-

mance of the reactor system, as shown in Table 1. The experiments were carried out to investigate the effect of power at two CH₄/O₂ ratios of 4:1 and 3:1. The input power was varied from 8 to 11 W. The conversions of methane and oxygen increased significantly with increasing power for both CH₄/O₂ ratios of 4:1 and 3:1. The highest power applied (11 W) was that above which the discharge became unstable due to carbon formation on both electrodes as well as the quartz tube wall. The results can be explained in that the main effect of increasing power on the AC electric gas discharge reactions results from increasing current. Therefore, it provides a higher electron production rate and more electrons are available to initiate the reactions. It was observed that the reactor wall temperature increased as the power increased. This temperature increase is simply related to the electric power dissipated. Power dissipation along with exothermic oxidation reactions contribute to increases in the bulk gas temperature, while the coupling reaction of methane is endothermic. It was found that an increase in power enhanced synthesis gas production, as the selectivities of both hydrogen and carbon monoxide increased. Under these conditions, sufficient high-energy electrons promote secondary reactions: the dehydrogenation of ethane to produce ethylene; ethylene is further dehydrogenated into acetylene resulting in a decrease in ethane selectivity along with increasing the selectivity of acetylene with increasing power. Interestingly, the H₂/CO ratio decreased significantly while the CO/C₂ ratio increased with increasing power. It was found that specific energy consumption decreased with increasing power.

Effect of Frequency. Frequency is another parameter affecting the discharge. It has been known that the main effects of frequency on the conversions and selectivities result from the space charge (electrons and ions) characteristics of the discharge, even though the power is constant. Table 2 shows the effect of frequency on partial oxidation of methane by varying frequency in the range of 200–700 Hz both with and without ethane. The maximum methane and oxygen conversions as well as the highest selectivities of carbon monoxide, acetylene, and hydrogen were found at 300 Hz. The selectivities of ethane and ethylene, and the specific energy consumption were found to be a minimum at the same frequency. At 300 Hz, there are the largest number of electrons available to activate methane to form all products as suggested by the increasing current from 0.3 to 0.39 A with decreasing frequency from 700 to 300 Hz. The streamer corona discharge generated by the AC electric field may be thought to be a temporary DC corona discharge, established within each half-cycle. The decay of the space charge is reduced with increasing frequency due to a faster reversal of the electric field. Acceleration of the remaining space charge by the reversing electric field decreases the amount of current needed to sustain the discharge. At high frequency, ethane is produced from coupling of methyl radicals. At a lower frequency, higher numbers of electrons result in more dehydrogenation of ethane and ethylene to acetylene and then to carbon oxides. The specific energy consumption increased with increasing frequency. Frequency in the study range has less effect on conversion and selectivity than power but frequency has a more

(40) Hill, B. J. M.S. Thesis, University of Oklahoma, Norman, OK, 1997.

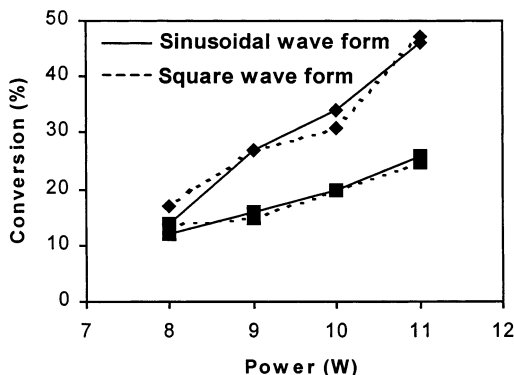


Figure 5. Effect of waveform on conversions of CH₄ (■) and O₂ (◆); CH₄/O₂ molar ratio, 3:1; overall flow rate, 100 cm³/min; gap distance, 10 mm; residence time, 0.23s; and applied frequency, 300 Hz.

significant effect on specific energy consumption than power. Below 300 Hz, carbon appears to form in the reactor. Since 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 reduction of both methane and oxygen conversions as well as the energy efficiency of the system.

Effect of Waveform. The effect of waveform was also investigated by using sinusoidal and square waveforms at a constant methane-to-oxygen ratio of 3:1 in the power range of 8–11 W for the CH₄/air system and 8–14 W for the CH₄/O₂/He system. The results are shown in Figure 5 and Table 3. Methane and oxygen conversions as well as product selectivities were not affected by the waveform. The difference of conversions and selectivities between the two waveforms was less than 5% for all experiments.

Conclusions

The results obtained from these studies show that a corona discharge could be an effective novel approach to produce synthesis gas from methane and air to reduce the cost of synthesis gas production in industrial applications. The operational parameters of CH₄/O₂ ratio, ethane addition, diluent gas, residence time, power, frequency, and waveform were investigated experimentally to understand their effects on the partial oxidation of methane to produce synthesis gas as well as C₂ hydrocarbons. Methane and oxygen conversions increased with increasing input power but decreased with increasing CH₄/O₂ feed mole ratio, flow rate and gap distance. The selectivity of ethane, produced from coupling of methane, changed opposite to methane conversion. Ethane reacts further by dehydrogenation to form ethylene and acetylene or by oxidation to produce carbon oxides. Current was constant with varying CH₄/O₂ ratio and flow rate while increasing with increasing input power and with decreasing gap distance and frequency. A frequency of 300 Hz and the highest power of each condition was the best to produce synthesis gas. With added ethane in the feed gas, the methane conversion dropped significantly but the oxygen conversion increased. Nitrogen was found to be a more effective diluent than helium as less energy was required to convert methane in the plasma environment. There was no distinguishable effect of changing the waveform between square and sinusoidal waveforms.

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