Partial Oxidation of Methane to Synthesis Gas by a Microwave Plasma Torch

Cheng-Hsien Tsai and Tsung-Hua Hsieh
Dept. of Chemical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan

Minliang Shih
Dept. of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan, Taiwan

Yuh-Jeen Huang
Dept. of Environmental and Safety Engineering, Chung-Hwa College of Medical Technology, Tainan, Taiwan

Ta-Chin Wei
Dept. of Chemical and Material Engineering, Chung Yuan University, Chung Li, Taiwan

DOI 10.1002/aic.10533
Published online July 18, 2005 in Wiley InterScience (www.interscience.wiley.com).

This study demonstrates a noncatalytic, low-pressure, and room-temperature process for methane partial oxidation into syngas by using a microwave plasma torch reactor. The experimental results showed that the elevation of the inlet O_2/CH_4 molar ratio, pressure, and applied power led to the outlet H_2/CO molar ratios decreased from 3.32 (at $O_2/CH_4 = 0.3$, 13.3 kPa, and 160 W) to 0.81 (at $O_2/CH_4 = 1.5$, 93.3 kPa, and 600 W). At $O_2/CH_4 = 0.5$, the higher selectivity and yield of syngas, and a H_2/CO molar ratio of about 2 could be obtained simultaneously. In addition, the maximum yield of syngas per unit mole of methane consumed could be achieved at a higher pressure, although a higher methane conversion was performed at a lower pressure. Based on these, this study suggests that the operating conditions of $O_2/CH_4 = 0.5$ and near atmospheric pressure (93.3 kPa) would be the most appropriate combination for converting methane into syngas. Under the conditions, the selectivities of H_2 and CO reached 97.6 and 99.2%, respectively, accompanied with $H_2/CO = 1.97$ at 600 W. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 2853–2858, 2005

Keywords: methane, conversion, syngas, microwave, plasma, energy

Introduction

For efficient conversion of energy resources, methane (CH_4) is generally used to produce the more valuable intermediates or products, such as synthesis gas (syngas, H_2 + CO), ethylene (C_2H_4), methanol (CH_3OH), and formaldehyde (CH_2O).[1–3] To convert CH_4 into syngas by partial oxidation ($CH_4 + 0.5O_2 \rightarrow CO + 2H_2$, $\Delta H^0_{298} = -59.7$ kJ/mol), steam reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$, $\Delta H^0_{298} = 229.7$ kJ/mol), and CO_2 reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$, $\Delta H^0_{298} = 247$ kJ/mol) reactions are the main route for subsequent methanol production, ammonia synthesis, or the Fischer–Tropsch synthesis.[4] It has been estimated that approximately 60–70% of the cost of the overall process is associated with syngas preparation in the process of methane conversion.[5] Moreover, the CH_4 conversion is based on the use of the highly active catalysts, such as

---

Correspondence concerning this article should be addressed to C.-H. Tsai at chtsai@cc.kuas.edu.tw.

© 2005 American Institute of Chemical Engineers

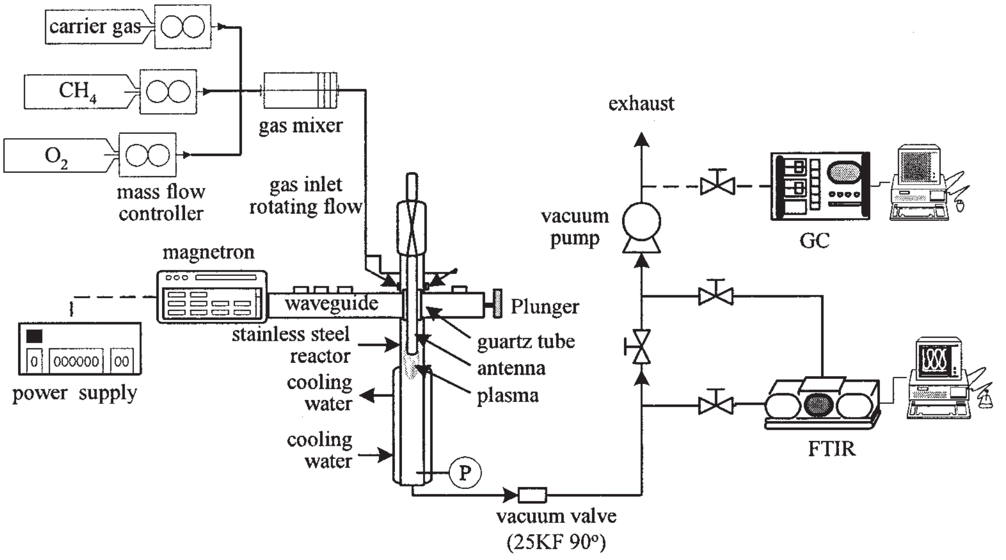

Figure 1. Microwave plasma system.

the Ni, Co, Ir, Pd, Pt, or Ru group metals supported on Al_2O_3, TiO_2, or oxidized diamond, at high temperature (1000–1300 K) and high pressure (15–30 atm) conditions.[4,5] Therefore, to develop a more economic and environmentally friendly alternative that can reduce the operating temperature, pressure, and avoid the problems of carbon depositions and catalyst poisons, we propose a new process.

The noncatalytic conversion of CH_4 or CH_4/O_2 has been carried out by the discharge approaches, such as high pulse frequency, corona, radio-frequency (rf), microwave (MW), and dielectric-barrier discharges (DBDs). However, these plasmas primarily yielded C_2 hydrocarbons, methanol, or diamond-like carbon film, not syngas.[6–11] Low-pressure rf plasma, which is usually used in industry for semiconductivity manufacture and surface modification, has been demonstrated for converting CH_4/O_2 into syngas in our preliminary study.[12] Although the high methane conversion and syngas selectivity has been achieved, the system operated at low pressure (4 kPa) and low flow rate [200 standard mL/min (sccm)] will restrict its practical use.

MW plasma, commonly used in microwave ovens, diamond deposits, and IC manufacture, has higher plasma density, electron mean energy, can be operated at a wide range of pressures and gas flow rates, and the advantages of easy operation and electrodeless reactor to avoid electrode erosion and contamination, make MW discharges more attractive than other plasmas. Thus, a MW plasma torch reactor with a single stage, noncatalytic process operated at various pressures was constructed to probe the key variations of products for partial oxidation of methane into syngas in this study.

Experimental

The experimental setup is shown schematically in Figure 1. The MW plasma system is assembled by a commercially available magnetron (Toshiba 2M130, 2.45 GHz) with maximum stationary power of 2 kW. The microwave is fed into an R26 waveguide, which is terminated by a movable plunger and connected laterally with a resonant auxiliary cavity. A quartz tube (ID, 4 cm; length, 7 cm) and an antenna (diameter, 1.6 cm; length, ~35 cm) are intersected perpendicularly by the waveguide and the resonator.

The flow rate of high-purity reactants, supplied from compressed gas cylinders, was adjusted with calibrated mass flow controllers, introduced into a gas mixer, and then injected tangentially into the top of the quartz tube. The well-mixed working gas, which passed through the quartz tube and entered the discharge zone of the reactor, enabled the stabilization of the plasma torch. After accomplishing the plasma-chemical reactions, the effluents flowed through the reactor equipped with an outer cooling tube in which the water passed in a direction opposite to that of the gas. Finally, the gas mixtures were analyzed and exhausted.

In the vertical cylindrical type, a stainless steel tube reactor (ID, 5 cm; length, 50 cm), the breakdown was initiated by enhancing the electromagnetic field to enable the MW plasma torch to discharge at the tip of the antenna. The discharge length was about 1–4 cm, although it was difficult to verify because of the stainless steel reactor, although a quartz window could be used to observe the discharge. By estimation, the gas residence time was in the range of 0.01 s (at 13.3 kPa, 1000 K, discharge length = 1 cm) and 0.34 s (at 93.3 kPa, 500 K, discharge length = 4 cm). After the plasma reactions were obtained, the final mixtures passed through the reactor that connected a KF 25 manually operated angle valve , to which was attached a mechanical vacuum pump to control the operating pressure.

Compositions of the products were identified and quantified by a gas chromatograph (Varian, GC3800, column type: SUPELCO 13821) equipped with a thermal conductivity detector for identifying CH_4, H_2, CO, CO_2, C_2H_2, C_2H_4, and C_2H_6. The analysis conditions of gas chromatography (GC) were as follows: injection temperature = 100°C, column temperature = 140°C, detector temperature = 270°C, and the flow rate of carrier gas = 30 sccm. In addition, an on-line Fourier transform infrared spectrometer (Avator 370, Nicolet Instrument Technologies) was also used to check the accuracy of GC analysis (except H_2) and to identify the trace amount of byproducts, such as CH_3OH, CH_2O, and C_2H_4. The FTIR analysis conditions were set as follows: resolution = 0.5 cm^{-1}, number of scans = 8, spectral range = 4000–400 cm^{-1}, gain = 4. H_2O was yielded in the experiments, although the concentrations were not measured in this study.

To check the gastight level of the system, the system pressure was pumped to lower than 1.3 Pa before any experiment was performed. After the plasma reactions were at steady state, the power and all inlet streams were turn off. Then N_2 was introduced to pass through the overall system to clean the contaminants and residues. Finally, the pressure was reduced to 1.3 Pa again until the next run was carried out.

The experimental conditions are summarized as follows: inlet O_2/CH_4 molar ratios (abbreviation: O_2/CH_4 or O_2/CH_4 ratio) were in the range of 0.3–1.5; system pressure (P) was operated at 13.3, 53.3, or 93.3 kPa; applied MW power (E) was set at 600 W (except assigned as 160 W); feeding concentration of CH_4 ($[CH_4]$) was kept at 5%; Ar was the carrier gas; temperature of the feed was at 303 K; total flow rate was fixed at 7000 sccm.

Results and Discussion

The compositions of products are based on molar fraction of the gaseous effluent. The conversion of CH_4 and the selectivities of H_2 (S_{H2}) and CO (S_{CO}) are calculated by the following equations

Conversion of CH_4

$$= (CH_4\text{ converted})/(CH_4\text{ fed to the reactor}) \times 100\%$$

$$S_{H_2} = 0.5H_2\text{ formed}/(CH_4\text{ converted}) \times 100\%$$

$$S_{CO} = CO\text{ formed}/(CH_4\text{ converted}) \times 100\%$$

where CH_4, H_2, and CO are, respectively, the moles of compounds CH_4, H_2, and CO.

Selectivities of H_2 and CO at different O_2/CH_4 ratios and values of P and E

S_{H2} and S_{CO} were examined at various O_2/CH_4 ratios because the factional factorial design method indicated that the O_2/CH_4 ratio dominated the selectivity of H_2 and CO.[12] Figure 2 shows that S_{H2} and S_{CO} increased with the elevation of operating pressure and applied power. The S_{H2} reached 99.9 and 97.6% at O_2/CH_4 = 0.3 and 0.5, respectively, at 93.3 kPa and 600 W. Similarly, the higher S_{CO} was achieved at O_2/CH_4 = 0.5, to be 99.2% at 93.3 kPa. Thus, the simultaneously higher S_{H2} and S_{CO} were found at O_2/CH_4 = 0.5 with higher pressure and applied power.

At O_2/CH_4 = 0.3, a lower S_{H2} was found (except at 93.3 kPa) than that at O_2/CH_4 = 0.5 because of the formation of the minor product, C_2H_2, although a large amount of H_2 was able to generate prominently at the oxygen-lean condition through the recombination of H atoms and the reactions of H with CH_4, OH, or HCO.[13,14] In addition, at a lower O_2/CH_4 ratio, a much greater S_{H2} was found at 600 W than that at 160 W, whereas at a higher O_2/CH_4 ratio, the S_{H2} was slight higher at 600 W than that at 160 W. By elevating the O_2/CH_4 ratio from 0.5 to 1.5 at 600 W, experimental results showed that S_{H2} decreased significantly from 89.7 to 28.4% at 13.3 kPa, as well as decreasing from 97.6 to 29.4% at 93.3 kPa (Figure 2a). The large amounts of H_2O, yielded at a higher O_2/CH_4 ratio, led to a reduction of H_2 selectivity.

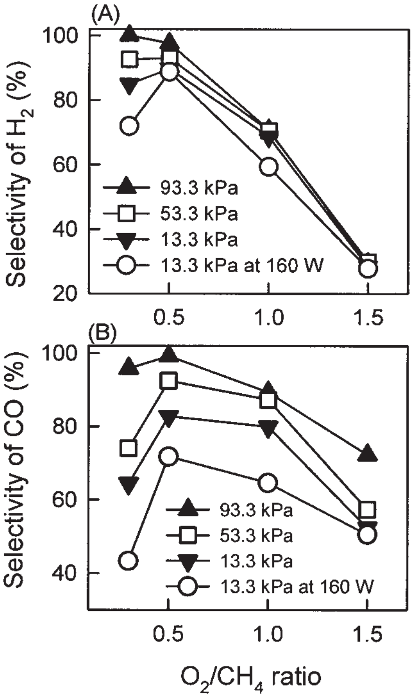

Figure 2. Selectivities of H_2 (A) and CO (B) for various inlet O_2/CH_4 ratios and pressures at 600 W (except otherwise assigned).

The selectivity of CO is also strongly dependent on the oxygen supply because CO is primarily formed by the following sequential reactions[13–15]

$$CH_3(+\,O) \rightarrow CH_2O(+\,e, O, H, OH) \rightarrow HCO(+\,O_2, O, H, OH) \rightarrow CO$$

Experimental results revealed that at increased O_2/CH_4 ratio or pressure, S_{CO} increased to a maximum value at O_2/CH_4 = 0.5 and then decreased, apparently because the addition of oxygen favors CO_2 formation by the reaction of CO with OH. Thus, when the O_2/CH_4 ratio increased from 0.5 to 1.5 at 600 W, S_{CO} decreased from 82.5 to 58.2% and from 99.2 to 75.8% at P = 13.3 and 93.3 kPa, respectively (Figure 2b). The results indicated this discharge approach might be adapted to operate at near atmospheric pressure not only to favor the syngas formation but also to save the consumption of pumping power.

Outlet H_2/CO molar ratios

The outlet H_2/CO molar ratios decreased drastically with increasing O_2/CH_4 ratio, and reduced slightly with increasing E or P (Figure 3). When the O_2/CH_4 ratio rose from 0.3 to 1.5, the H_2/CO ratios decreased from 3.32 to 1.10 at 13.3 kPa and 160 W, and reduced from 2.11 to 0.81 at 93.3 kPa and 600 W. The

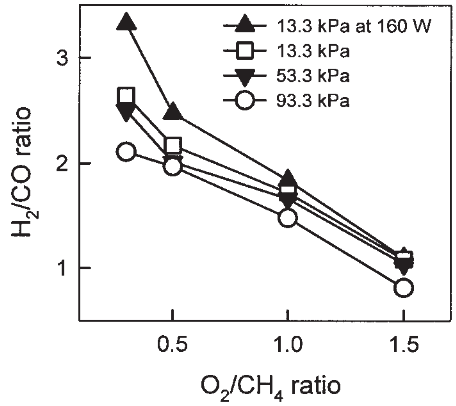

Figure 3. Outlet H_2/CO molar ratios for various inlet O_2/CH_4 ratios and pressures at 600 W.

H_2/CO ratios decreased with increasing O_2/CH_4 ratio, to indicate that the formation of H_2O is predominant over that of CO_2 in the O_2-containing plasma condition.

Notably, the H_2/CO ratios remained at approximately 2 when the O_2/CH_4 ratio was 0.5, to equal 1.97, 2.01, and 2.17 at 93.3, 53.3, and 13.3 kPa, respectively, at 600 W (Figure 3). Syngas with H_2/CO ratio of 2 is suitable to serve as an intermediate for directly converting syngas into fuels and chemicals, including the CH_3OH synthesis ($2H_2 + CO = CH_3OH$) and the Fisher–Tropsch reaction. Besides, even at O_2/CH_4 ratio $\ll 0.5$, when *P* is operated at a lower condition, a hydrogen-rich ($H_2/CO > 3$) syngas provides the other flexible process, such as the manufacture of hydrogen gas by the water–gas shift reaction ($CO + H_2O = CO_2 + H_2$), and further used to synthesize NH_3.

Conversion of methane at various O_2/CH_4 ratios and values of P and E

Figure 4 shows that increasing the O_2/CH_4 ratio or *E*, as well as reducing *P*, apparently could enhance the CH_4 conversion. When the O_2/CH_4 ratio increased from 0.3 to 1.5 at 600 W, the conversion of CH_4 increased from 39.1 to 69.7% at 53.3 kPa, and from 28.6 to 65.5% at 93.3 kPa, thus indicating that the addition of oxygen significantly improved the methane conversion. The active species produced from the plasmalysis of O_2 yielded CO, CO_2, and H_2O, which not only oxidized CH_4 to enhance the conversion by the reaction, such as $CH_4 + O \rightarrow CH_3 + OH$, but also inhibited the recombination of methane and the formation of C_2 hydrocarbons. In addition, a higher value of *E*, accompanied by a larger plasma density, enhanced the probability of the impact–dissociation reactions to result in the increase of CH_4 conversion. Figure 4 shows that at 13.3 kPa, to elevate *E* from 160 W to 600 W, the conversion of CH_4 increased from 37.6 to 66.3% at $O_2/CH_4 = 0.3$, and from 70.6 to 90.9% at $O_2/CH_4 = 1.5$.

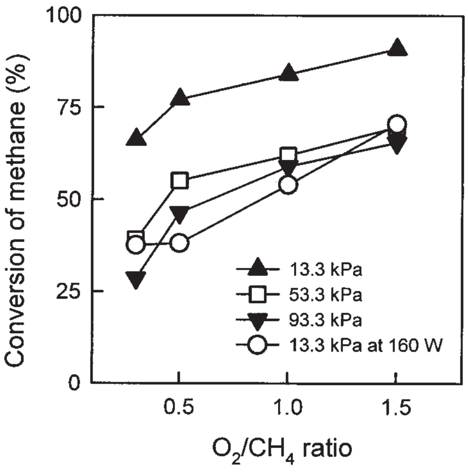

Figure 4. Conversions of methane under various inlet O_2/CH_4 ratios and pressures at 600 W.

Table 1. Energy Efficiency (μmol/J) at Different Inlet O_2/CH_4 Molar Ratios, Operating Pressures, and Applied Powers

O_2/CH_4 Ratio	160 W 13.3 kPa	600 W 13.3 kPa	600 W 53.3 kPa	600 W 93.3 kPa
0.3	0.56	0.26	0.16	0.11
0.5	0.57	0.31	0.22	0.18
1.0	0.81	0.33	0.25	0.23
1.5	1.05	0.36	0.28	0.26

However, when *P* increased from 13.3 to 93.3 kPa at 600 W, CH_4 conversion decreased from 77.2 to 46.4% at $O_2/CH_4 = 0.5$, and from 84.0 to 60.7% at $O_2/CH_4 = 1$ (Figure 4). At a higher *P*, a greater gas density increased the probability of collisions, whereas the shorter mean free path of electrons resulted in the reduction of electron temperature prevented the effective impact dissociation of CH_4.

Table 1 lists the energy efficiency (moles of CH_4 converted per joule), which could reach 1.05 μmol/J at 160 W, $O_2/CH_4 = 1.5$ and 13.3 kPa, whereas the energy efficiency decreased to 0.11 μmol/J at 600 W, 93.3 kPa, and $O_2/CH_4 = 0.3$. In comparison with the other plasma conversion approaches, the energy efficiency in this study is similar to that of the others, such as CH_4 conversion to C_2 (ethane, ethylene, and acetylene) using MW plasma (0.22–0.34 μmol/J)[16]; CH_4/O_2 conversion using pulsed AC dielectric-barrier discharges (0.36 μmol/J)[17]; CH_4/O_2 conversion using silent discharges (0.37 μmol/J)[18]; and CH_4/O_2 conversion to CH_3OH/CH_2O using pulsed-discharge plasma (0.7 μmol/J),[19] which is much lower than CH_4/CO_2 conversion to $CO/H_2/C_2$ using pulsed MW plasma [1.56 μmol ($CH_4 + CO_2$)/J] or high-frequency pulsed plasmas [2–3 μmol ($CH_4 + CO_2$)/J].[17,20] Thus, the energy efficiency of this study is moderate, and will be further improved in the future, such as by using a relatively high [CH_4] at a high temperature of input gas mixture, a modified reactor structure, and by adding a third component such as CO_2 or H_2O, although the present energy efficiency is far from the level for industrial application.

Maximum yield of syngas—the optimal operating conditions

Figure 5 shows that the maximum molar fractions of H_2 and CO were attained at $O_2/CH_4 = 0.5$ and 1, respectively, with a lower *P* (13.3 kPa) and a higher *E* (600 W). The results showed that the molar fraction of syngas did not decrease, although the conversion of CH_4 was lower at a lower O_2/CH_4 ratio. The maximum molar fraction of H_2 was 6.92 and 4.53% at 13.3 and

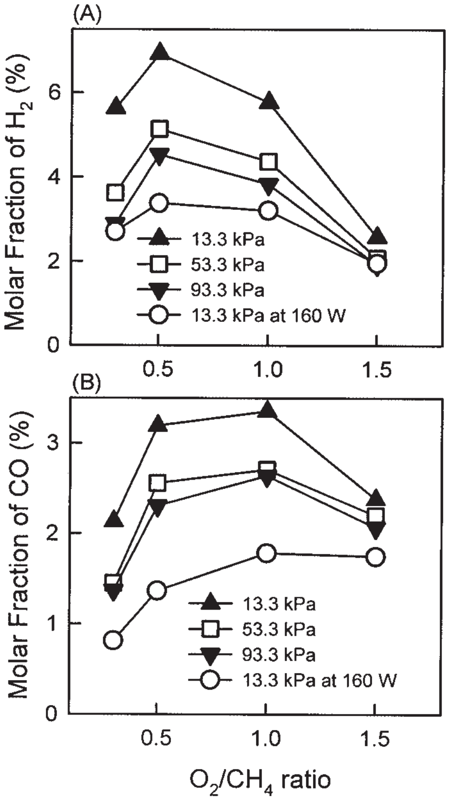

Figure 5. Molar fractions of H_2 (A) and CO (B) for various inlet O_2/CH_4 ratios and pressures at 600 W.

93.3 kPa, respectively (Figure 5a), under the condition of $O_2/CH_4 = 0.5$. Meanwhile, other H-containing byproducts were hardly observed. However, a small amount of C_2H_2 was formed at $O_2/CH_4 = 0.3$ and a substantial amount of H_2O was produced at O_2/CH_4 ratio > 1, which explained the reduction of $[H_2]$. As for CO, the maximum molar fraction was found at $O_2/CH_4 = 1$, to reach 3.36 and 2.64%, at 13.3 and 93.3 kPa, respectively (Figure 5b) because a poor CH_4 conversion was achieved at $O_2/CH_4 = 0.5$, and a large amount of CO_2 was formed at O_2/CH_4 ratio > 1.

Although the energy efficiency reached a maximum value at $O_2/CH_4 = 1.5$ with lower values of E and P, poor S_{H2}, S_{CO}, and a very low H_2/CO ratio were found as a result of the formation of large amounts of H_2O. However, the experimental results showed that the higher H_2/CO ratio, S_{H2}, S_{CO}, and yield of H_2 were found at $O_2/CH_4 = 0.5$ than at $O_2/CH_4 = 1$, whereas the higher CH_4 conversion and CO yield were found for $O_2/CH_4 = 1$ than at $O_2/CH_4 = 0.5$. Thus, the maximum amounts of syngas produced should be examined between O_2/CH_4 values of 0.5 and 1. The total molar fraction of syngas and the syngas yield are used and defined as follows

$$\text{Total molar fraction of syngas} = [H_2] + [CO] \qquad (\%)$$

$$\text{Syngas yield} = (\text{moles of } H_2 \text{ and CO formed})/(\text{moles of } CH_4 \text{ converted})$$

From Figure 5, a simple calculation denotes that the maximum total molar fraction of syngas is 10.1% at $O_2/CH_4 = 0.5$, 13.3 kPa and 600 W, greater than 6.83% at $O_2/CH_4 = 0.5$, 93.3 kPa, and 600 W, to indicate that operating the MW plasma at $O_2/CH_4 = 0.5$ with a lower P value seems a better choice. However, the maximum syngas yield, which means the most energy efficient, is also found at $O_2/CH_4 = 0.5$, reaching 2.94 at 93.3 kPa, whereas it is 2.62 at 13.3 kPa. Thus, the results suggest that a high yield of syngas could be achieved near atmospheric pressure to favor the practical application.

Byproduct compositions

MW discharge can generate energetic electrons to result in high dissociation ratios. An abundance of free radicals is produced by the electron impaction–dissociation of CH_4 and O_2 according to the following reactions[13,21–23]

$$CH_4 \rightarrow CH_3 + H \quad \text{or} \quad CH_2 + H_2 \quad \text{or} \quad CH + H_2 + H$$

$$O_2 \rightarrow O + O$$

These species then further react with each other to form many stable products. Thus, the byproducts should be identified, especially at various O_2/CH_4 ratios, because the $[O_2]$ dominated the product compositions.[12] Experimental results revealed that H_2, CO, CO_2, H_2O, and C_2H_2 were the major components. Meanwhile, traces of CH_2O and CH_3OH, which can be generated mainly by the reactions of $CH_3 + O$ and $CH_3 + OH$, respectively, are easily dissociated again because of the weak bonds, resulting in their detection only at conditions of lower O_2/CH_4 ratio and E. Interestingly, C_2H_4 and C_2H_6 were not observed, although C_2 compounds were the major products in both the CH_4 rf and the $CH_4/H_2/O_2$ AC plasmas.[13,24]

Although the stoichiometric ratio of O_2/CH_4 equaled 0.5 ($0.5O_2 + CH_4 \rightarrow CO + 2H_2$) for producing syngas, the product compositions showed that at O_2/CH_4 ratio < 1, syngas was the major product, and at $O_2/CH_4 = 1$, H_2O and CO were the major compounds and H_2 and CO_2 were the minor products. At O_2/CH_4 ratio > 1.5, CO_2 and H_2O were the main products because of their high thermodynamic stability in an oxygen-rich environment.

The formation pathways of C_2H_2 are usually by the $CH + CH_4 \rightarrow C_2H_4 + H$ reaction, and then C_2H_4 was dissociated as C_2H_2 and H (or H_2) in the plasma system. Figure 6 shows that the molar fraction of C_2H_2 decreased from 0.562% to 0 at 13.3 kPa when the O_2/CH_4 ratio increased from 0.3 to 1.5 at 600 W and indicated that C_2H_2 was yielded at a lower P with an oxygen-lean condition. In addition, C_2H_2 could not be detected at 93.3 kPa, which favors the MW plasma torch being operated at a higher P.

CO_2 is the most stable product in an oxygen-rich condition. To add oxygen will yield OH radical and favor the $CO + OH \rightarrow CO_2 + H$ reaction, to lead to the reduction of S_{CO}.[13] Figure 6 shows that the molar fraction of CO_2 apparently increased from 0.045 to 1.71% at 13.3 kPa, and increased only from 0.016 to 0.754% at 93.3 kPa, by increasing the O_2/CH_4 ratio from 0.3 to 1.5 at 600 W.

No obvious carbon black or depositions, which will cause a

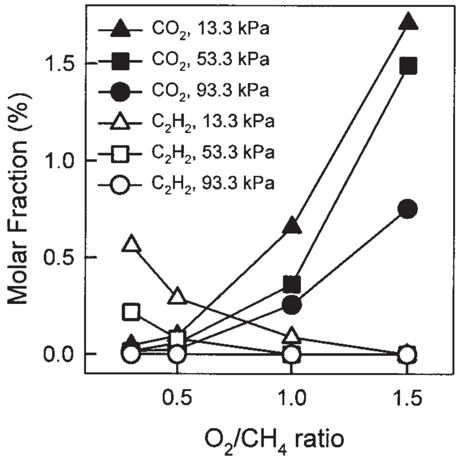

Figure 6. Molar fractions of C_2H_2 and CO_2 for various inlet O_2/CH_4 ratios and pressures at 600 W.

fouling problem, were observed. Moreover, no complex molecules such as C_3-hydrocarbons were detected. The active species, such as radicals, have a short lifetime and quenching time of only several miniseconds, limit the probabilities of formation of complex compounds in the afterglow zone.

In conclusion, under large flow rate, room-temperature, and no-catalyst conditions, methane/oxygen is successfully converted into syngas by a microwave plasma reactor. Syngas, with comprehensive ranges of H_2/CO molar ratios, can be conveniently produced just by adjusting primarily the inlet O_2/CH_4 molar ratios. The optimal operating condition was at $O_2/CH_4 = 0.5$, which had a H_2/CO ratio of approximately 2. At a lower pressure (13.3 kPa), the maximum CH_4 conversion and total molar fractions of H_2 and CO were obtained. However, the most economic utility rate of reactants [that is, the maximum syngas yield could reach 2.94 (mole of syngas/mole of CH_4 consumed] was when the MW plasma reactor was operated at 93.3 kPa. The results suggest that the plasma torch reactor may be practically operated near atmospheric pressure.

Acknowledgments

We thank the National Science Council in Taiwan for the financial support of this research work under Grant NSC 91-2218-E-151-001.

Literature Cited

1. Periana RA, Taube DJ, Evitt ER, Loffler DG, Wentrcek PR, Voss G, Masuda T. A mercury-catalyzed, high-yield system for the oxidation of methane to methanol. *Science.* 1993;259:340-343.
2. Ashcroft AT, Cheetham AK, Foord JS, Green MLH, Grey CP, Murrell AJ, Vernon PDF. Selective oxidation of methane to synthesis gas using transition metal catalysts. *Nature.* 1990;344:319-321.
3. Spencer ND, Pereira CJ. Partial oxidation of CH_4 to HCHO over a MoO_3-SiO_2 catalyst: A kinetic study. *AIChE J.* 1987;33:1808-1812.
4. Nakagawa K, Nishimoto H, Kikuchi M, Egashira S, Enoki Y, Ikenaga N, Suzuki T, Nishitani-Gamo M, Kobayashi T, Ando T. Synthesis gas production from methane using oxidized-diamond-supported group VIII metal catalysts. *Energy Fuels.* 2003;17:971-976.
5. Zaman J. Oxidative processes in natural gas conversion. *Fuel Process Technol.* 1999;58:61-81.
6. Fincke JR, Anderson RP, Hyde TA, Detering BA. Plasma pyrolysis of methane to hydrogen and carbon black. *Ind Eng Chem Res.* 2002;41:1425-1435.
7. Yao SL, Nalayama A, Suzuki E. Methane conversion using a high-frequency pulsed plasma: Important factors. *AIChE J.* 2001;47:413-418.
8. Yao SL, Suzuki E, Nakayama A. The pyrolysis property of a pulsed plasma of methane. *Plasma Chem Plasma Process.* 2001;21:651-663.
9. Tanaka KI, Mutsukura N. Deposition of diamond-like carbon film and mass spectrometry measurement in CH_4/O_2 RF plasma. *Plasma Chem Plasma Process.* 1999;19:217-227.
10. Zhou LM, Xue B, Kogelschatz U, Eliasson B. Partial oxidation of methane to methanol with oxygen or air in a nonequilibrium discharge plasma. *Plasma Chem Plasma Process.* 1998;18:375-393.
11. Oumghar A, Legrand JC, Diamy AM, Turillon N, Ben-Aim RI. A kinetic study of methane conversion by a dinitrogen microwave plasma. *Plasma Chem Plasma Process.* 1994;14:229-249.
12. Tsai CH, Hsieh TH. New approach for methane conversion using an RF discharge reactor. 1. Influences of operating conditions on syngas production. *Ind Eng Chem Res.* 2004;43:4043-4047.
13. Fan WY, Knewstubb PF, Kaning M, Mechold L, Ropcke J, Davies PB. A diode laser and modeling study of mixed (CH_4–H_2–O_2) AC plasmas. *J Phys Chem A.* 1999;103:4118-4128.
14. Tsang W, Hampson RF. Chemical kinetic data base for combustion chemistry. Part I. Methane and related compounds. *J Phys Chem Ref Data.* 1986;15:1087-1090.
15. Zhou LM, Xue B, Kogelschatz U, Eliasson B. Nonequilibrium plasma reforming of greenhouses gases to synthesis gas. *Energy Fuels.* 1998b;12:1191-1199.
16. Suib SL. A direct, continuous, low-power catalytic conversion of methane to higher hydrocarbons via microwave plasmas. *J Catal.* 1993;139:383-391.
17. Zhang JQ, Zhang JS, Yang YJ, Liu Q. Oxidative coupling and reforming of methane with carbon dioxide using a pulsed microwave plasma under atmospheric pressure. *Energy Fuels.* 2003;17:54-59 (and references cited therein).
18. Larkin DW, Lobban LL, Mallinson RG. Proc of 1st International Conference on Gas Processing, AIChE Spring National Meeting, Atlanta, GA, March 5–9; 2000:10.
19. Okumoto M, Kim HH, Takashima K, Katsura S, Mizuno A. Reactivity of methane in nonthermal plasma in the presence of oxygen and inert gases at atmospheric pressure. *IEEE Trans Ind Appl.* 2001;37:1618-1624.
20. Yao SL, Okumoto A, Nakayama A, Suzuki E. Plasma reforming and coupling of methane with carbon dioxide. *Energy Fuels.* 2001c;15:1295-1299.
21. Mechold L, Ropcke J, Duten X, Rousseau A. On the hydrocarbon chemistry in a H_2 surface wave discharge containing methane. *Plasma Sources Sci Technol.* 2001;10:52-60.
22. Shimozuma M, Tochitani G, Tagashira H. Optical emission diagnostics of $H_2 + CH_4$ 50 Hz–13.56 MHz plasmas for chemical vapor deposition. *J Appl Phys.* 1991;70:645-648.
23. Itoh H, Taheyama Y, Ikeda M, Satoh K, Nakao Y, Tagashira H. Spectroscopic and image intensified investigations of RF plasmas in H_2 and CH_4 mixtures. *IEE Proc Sci Meas Technol.* 1994;141:95-98.
24. Hsieh LT, Lee WJ, Chen CY, Chang MB, Chang HC. Converting methane by using an RF plasma reactor. *Plasma Chem Plasma Process.* 1998;18:215-239.

Manuscript received Aug. 4, 2004, and revision received Feb. 18, 2005.