

Direct Conversion of Methane into Methanol and Formaldehyde in an RF Plasma Environment II: Effects of Experimental Parameters

Ya-Fen Wang^{a*}, Cheng-Hsien Tsai^b, Minliang Shih^c, Lien-Te Hsieh^d and Wen-Ching Chang^c

^a*Department of Bioenvironmental Engineering, Chung Yuan Christian University, No. 200, Chung Pei Road, Chung-Li 320, Taiwan*

^b*Department of Chemical Engineering, National Kaohsiung University of Applied Sciences, No. 415, Chien Kung Road, Kaohsiung 807, Taiwan*

^c*Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, No. 60, Sec. 1, Erh-Jen Road, Tainan 717, Taiwan*

^d*Department of Environmental Engineering and Science National Pingtung University of Science and Technology, 1Hseuh Fu Rd., Nei Pu Hsiang, Ping Tung, 912, Taiwan*

Abstract

To provide information on the conversion of methane in a non-catalyzed radio-frequency (RF) plasma system into valuable chemicals, such as HCHO, CH₃OH, C₂H₆, C₂H₄ and C₂H₂, an experiment was conducted to convert methane directly into methanol and formaldehyde. The effects of experimental parameters—specific energy (power or flow variation) and CH₄ and O₂ feeding concentrations—were examined. Carbon-based by-products generated in a CH₄/O₂/Ar RF plasma system included CO, CO₂, HCHO, CH₃OH, C₂H₆, C₂H₄ and C₂H₂. The methane conversion ratio increased as the feeding concentration of O₂ and the specific energy was increased, but decreased with feeding of CH₄. Increasing power in the RF plasma system did not favor the partial oxidation of CH₄ toward CH₃OH and HCHO, but did favor the production of C₂-hydrocarbons (C₂H₆, C₂H₄ and C₂H₂), CO, and CO₂. The CH₄ feeding concentration of under 15% or an O₂ content of under 10% favored the formation of CH₃OH and HCHO. CO concentration decreased as the feeding concentration of CH₄ increased, and increased as the feeding concentration of O₂ increased. The yield of CH₃OH was less than 1%. No carbon black or deposition was observed. Further research will seek to increase the yield of CH₃OH and HCHO by adding catalysts to the system.

* Corresponding author. Tel: +886-3-2654904 ; Fax: +886-3-2654949

E-mail address: yfwang@cycu.edu.tw

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INTRODUCTION

Due to the cost and risk of producing, handling, shipping, and storing hazardous chemicals the chemical industry has avoided using them as raw materials in chemical synthesis. Some alternatives to their use also are major generators of environmentally harmful waste, which raises serious safety concerns (Shreiber et al., 1996, 1999). A new approach to the problem of using hazardous and reactive chemicals is in-situ generation; moreover, C₂-hydrocarbon by-products (C₂H₆, C₂H₄ and C₂H₂) are industrially important and are useable as raw materials or as fuels (Okumoto and Mizuno, 2001; Okazaki et al., 1997). Regarded as a highly desirable fuel and alternative chemical feedstock, natural gas supplies more energy per CO₂ molecule created than oil does; thus helping to mitigate global warming, particularly when the methane in natural gas is converted directly into methanol (Lange, 1997). Among the carbon-based by-products generated in this study—CO, CO₂, HCHO, CH₃OH, C₂H₆, C₂H₄ and C₂H₂—CH₃OH, which is a promising clean fuel for the future, and syngas (CO+H₂), as a feedstock, can be converted into a liquid fuel by the Fischer-Tropsch process, or converted to methane, methanol, ammonia and other chemicals. HCHO is a versatile intermediate and a basic building block of several chemicals with various end uses, including wood products, coatings and resins.

Traditionally, the production of methanol from methane proceeds in two steps—the formation of syngas (CO + H₂), then subsequent reactions, such as F-T synthesis, to form methanol (Tsang et al. 1995). In this study the characteristics of the conversion of methane using the RF (radio frequency) plasma method were measured in order to offer a better understanding of the parameters that affect homogeneous gas-phase reaction. Those parameters include specific energy, and CH₄ and O₂ feeding concentration, all of which impact the input of total carbon converted into CH₃OH (F_{CH₃OH}), HCHO (F_{HCHO}) and C₂H₂ + C₂H₄ + C₂H₆ (F_{C₂}). The carbon balance in all experiments was between 0.87 and 1.24. Notably, no carbon black or deposition was observed during the process. The one-step oxidation of methane into methanol, formaldehyde, ethane, ethylene, and acetylene markedly reduces the costs of the process and provides an alternative to reducing the concentration of the global warming gas, methane, in the atmosphere.

EXPERIMENTAL SECTION

The apparatus used in this experiment is depicted schematically in a preliminary study and elsewhere (Tsai et al. 2003). A diffusion pump (Pfeiffer, DUO 065 DC) was used to maintain the system pressure below 0.0013 mbar to prevent pre-experimental contamination. CH₄, O₂ and Ar were metered using Brooks type 5850E mass flow controllers at a total flow of 100 cm³.min⁻¹ and introduced separately into

the reactor (4.5 cm I.D. × 15 cm height). The inside of the reactor was separated into two sections by a glass plate to separate the input gases, CH₄ and O₂, before they were recombined in the reactor's effluent. A plasma generator (PFG 600 RF, Fritz Huttinger Elektronik GmbH), operating at 13.56 MHz, with a matching unit (Matchbox PFM) produced the RF plasma discharge. The reactants and final mixtures were analyzed by an on-line Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet AVATRA 360), which was used to determine the amounts of CH₄, CH₃OH, HCHO, C₂H₂, C₂H₄, C₂H₆, CO and CO₂. A gas chromatograph (GC, HP 5890A) equipped with a thermal conductivity and flame photometric detector was also used to identify reactants and products. The accuracy of the results was also determined using a carbon mass balance. Under each experimental condition, the applied power, CH₄, O₂ and Ar feeding concentrations and operational pressures were measured more than three times to ensure that the system remained in a steady-state. All experiments were performed by setting the operational parameters and design conditions as follows: the feeding concentrations of CH₄ ([CH₄]_{in}) and O₂ ([O₂]_{in}) were kept at 2-30% and 1-40%, respectively, with inlet [CH₄]/[O₂] ratios of 0.13-5.0 and total flow rates of 20-100 cm³.min⁻¹; the RF power levels were applied within the 30–150W range at room temperature (25°C); and the operational pressure was 13.3 mbar to generate discharge at low effluent gas temperatures, which were measured using a thermocouple at the rear of the discharge zone.

RESULTS AND DISCUSSION

SPECIFIC ENERGY

The specific energy, measured in kWh/Nm³ of feed gas, was varied by changing either the applied power or the flow rate. Applied power significantly affected the conversion ratio in the plasma reactor, as previous studies have demonstrated (Zhu et al. 1992; Wang et al. 2000). Sustaining the RF plasma required sufficient energy to maintain ionization, which depended on the amount of energy supplied (Rossnagel et al. 1990). Figure 1 illustrates that X_{CH₄} increased with specific energy. The general trends in X_{CH₄} with a specific energy were very similar at various applied powers and total flow rates. The initial reactions in the plasma reactor involved the excitation of Ar as follows:



In the CH₄/O₂/Ar system, O₂ can be dissociated and excited as follows:



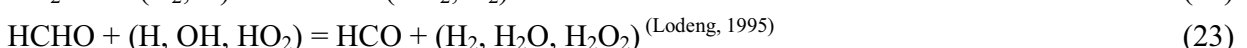
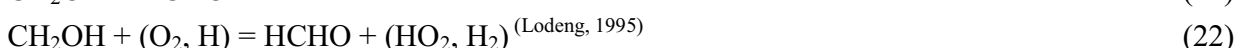
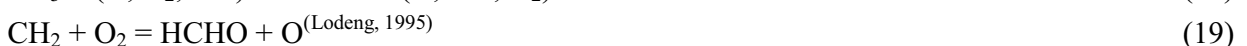
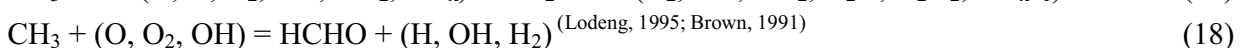
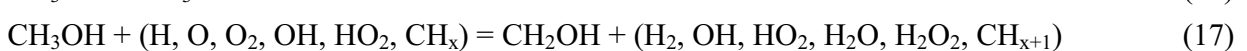
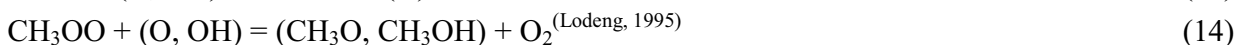


Moreover, CH₄ can be directly ionized, attached, or dissociated by electron-impact.

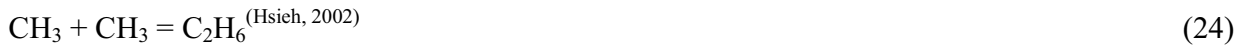


M indicates a third molecule, an energy-carrier which did not change chemically between collisions in the RF plasma reactor during the reaction process. A higher applied power and a higher temperature will shift the Maxwell-Boltzmann velocity distribution toward higher speeds, and thus higher energies (Wang et al., 1999). Hence, the conversion ratio of methane increased with the applied power.

Figure 2 indicates that F_{CH₃OH} and F_{HCHO} declined as the specified energy was increased; however, F_{C₂} increased with specific energy. The influence on F_{CH₃OH}, F_{HCHO} and F_{C₂} above 12 kWh.Nm⁻³ - especially on F_{HCHO} - of increasing the applied power was much stronger than that of reducing the total flow rate. At a given specific energy, a higher applied power did not favor the partial oxidation of CH₄ to CH₃OH and HCHO in the RF plasma system. A higher applied power inhibited the production or favored the decomposition of CH₃OH and HCHO, as follows.



However, a higher applied power favored the formation of higher hydrocarbons:

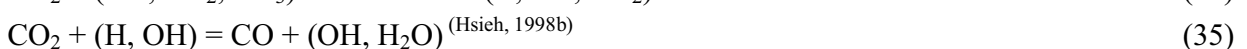


Interestingly, F_{C_2} exceeded $F_{\text{CH}_3\text{OH}}$, F_{HCHO} above 15 kWh.Nm⁻³ at various applied powers, possibly because the probability associated with CH_x radicals colliding with each other greatly exceeded that of colliding with oxygen-containing radicals, because many more CH_x radicals were generated as the applied power was increased. However, this probability changes with total flow rate. $F_{\text{CH}_3\text{OH}}$, F_{HCHO} and F_{C_2} changed only a little after 15 kWh.Nm⁻³ at various total flow rates. Reducing the total flow rate reduced the concentration of Ar, making the transfer of energy in the RF plasma system less inefficient, and possibly favoring the formation of CH₃O and CH₃OO radicals, as in CH₃ + (O, O₂) = (CH₃O, CH₃OO)—or it led directly to the formation of HCHO, as in (CH₃, CH₂, C₂H₃) + O₂ = HCHO + (OH, O, CHO).

CO was the main product in the experiment. Figure 3 showed that F_{CO} increased by a factor of 2.74 for specific energies at various applied powers from 5.0 to 30.0 kWh.Nm⁻³, but increased by a factor of 2.36 times for specific energies from 5.0 to 33.3 kWh.Nm⁻³ at various total flow rates. Increasing the applied power favored the formation of CO.



The increment of F_{CO} for various applied powers exceeded that for various total flow rates. However, this was not the case for F_{CO_2} , which increased by a factor of 4.86 for specific energies from 5.0 to 33.3 kWh.Nm⁻³ at various total flow rates, and reached a maximum of 8.3 kWh.Nm⁻³ for various applied powers. The steady state was maintained at around 12% when specific energy exceeded 10.0 kWh.Nm⁻³. The formation and decomposition of CO₂ may have proceeded as follows.



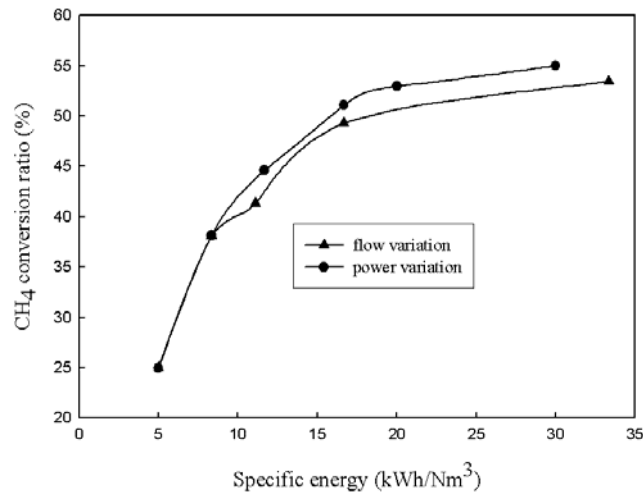


Figure 1. Influence of the specific energy on CH₄ conversion ratio (O₂/CH₄ = 1.0, power variation, flow rate = 100sccm, flow variation, applied power = 50 W).

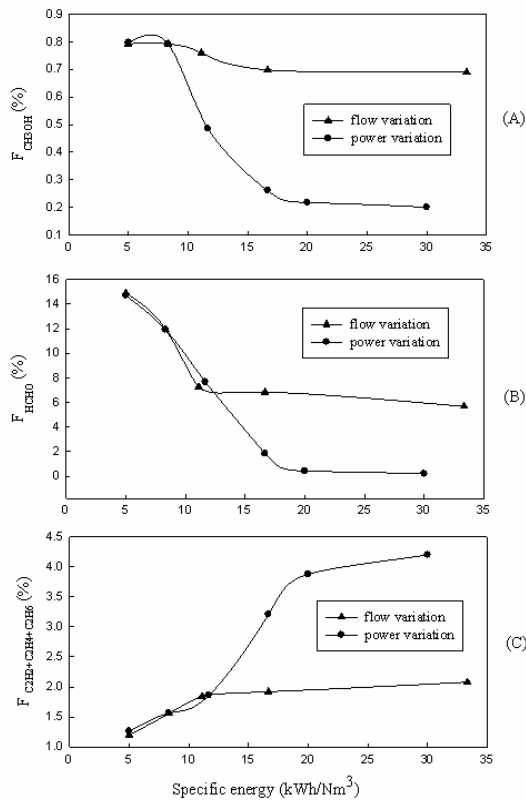


Figure 2. Influence of the specific energy on (A) F_{CH₃OH} (%) (B) F_{HCOH} (%) (C) F_{C₂H₂+C₂H₄+C₂H₆} (%) (O₂/CH₄ = 1.0, power variation, flow rate = 100sccm, flow variation, applied power = 50 W).

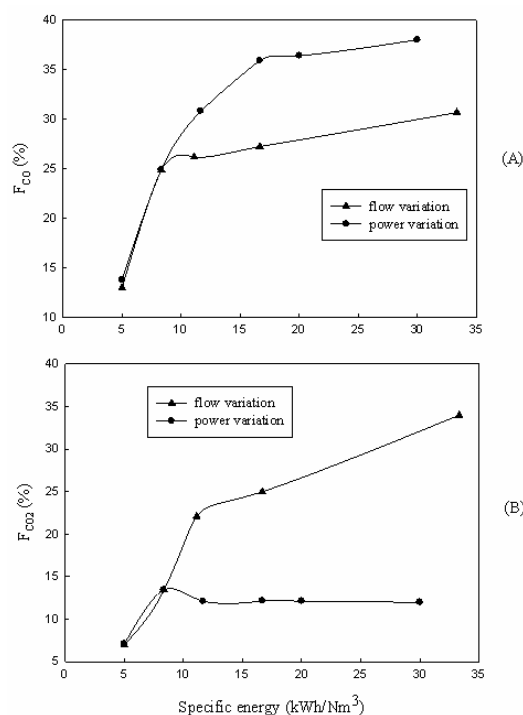


Figure 3. Influence of the specific energy on (A) F_{CO} (%) (B) F_{CO₂} (%) (O₂/CH₄ = 1.0, power variation, flow rate = 100sccm, flow variation, applied power = 50 W).

The formation of CO competed with that of CO₂, as the specific energy was increased at various total flow rates, especially above 15.0 kWh.Nm⁻³. However, changing the applied power did not cause this competition. Increasing the applied power apparently favored the formation of CO, but inhibited the production of CO₂. The formation and decomposition of CO₂ was balanced dynamically while the specific energy exceeded 10 kWh.Nm⁻³.

CH₄ FEEDING CONCENTRATION

Figure 4 plots the effect of the CH₄ feeding concentration on the CH₄ conversion ratio. X_{CH₄} increased by a factor of 1.20 times as applied power increased from 50 to 100 W at a 2% CH₄ feeding concentration, and increased by a factor of 2.25 as applied power increased from 50 to 100 W at a 30% CH₄ feeding concentration. The decreasing CH₄ conversion ratio was due to the fixed power supply in the system. More competition in the fixed volume reactor resulted in reducing the conversion ratio. Furthermore, Figure 5(a) shows that F_{CH₃OH} reached its maximum, 0.92 and 0.86%, at CH₄ feeding concentrations of 10% and 20% for applied powers of 50 W and 100 W, respectively. Notably, no CH₃OH was formed at a CH₄ feeding concentration under 4% for an applied power of 50 W. The

increasing CH₄ feeding concentration might favor the reaction of CH₄ + CH₃O = CH₃ + CH₃OH and led to the increasing CH₃OH concentration; however, elevated CH_x radicals from the increasing CH₄ feeding concentration might also have elevated the reaction rate of CH₃OH + CH_x = CH₂OH + CH_{x+1} and reached a dynamic balance in the RF plasma system. Figure 5(b) indicates that F_{HCHO} initially increased and reached a maximum, 18.5 and 6.28%, at a feeding concentration of CH₄ of 15% and 20% at applied

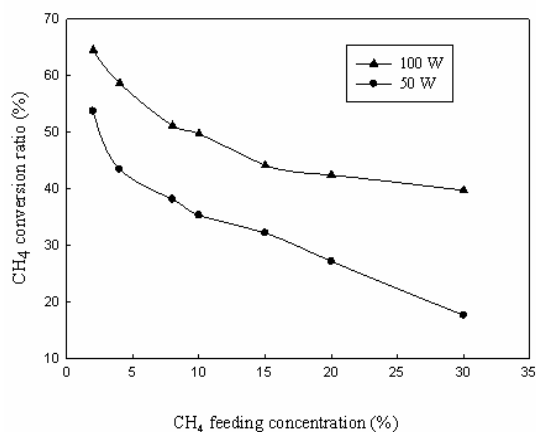


Figure 4. Influence of CH₄ feeding concentration on CH₄ conversion ratio (O₂/CH₄ = 1.0, total flow rate = 100sccm).

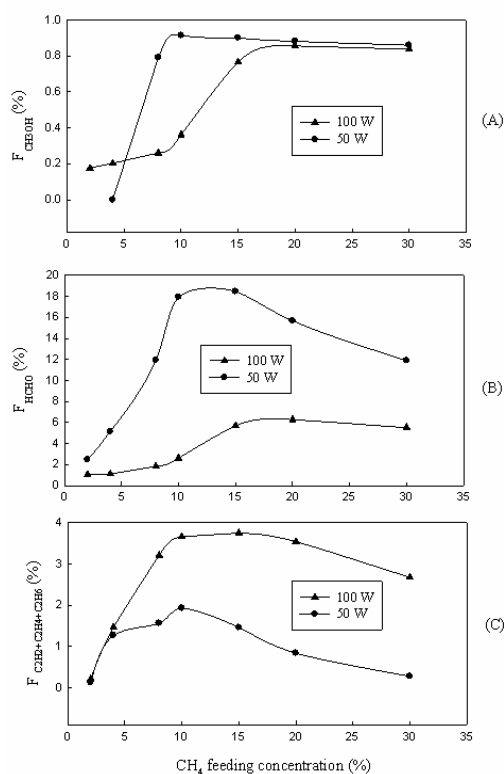


Figure 5. Influence of the CH₄ feeding concentration on (A) F_{CH₃OH} (%) (B) F_{HCHO} (%) (C) F_{C₂H₂+C₂H₄+C₂H₆} (%) (O₂/CH₄ = 1.0, total flow rate = 100sccm).

powers of 50 W and 100 W respectively before declining to 11.9 and 5.52% at a CH₄ feeding concentration of 30% at applied powers of 50 W and 100 W, respectively. Increasing the CH₄ feeding concentration resulted in the generation of more CH_x radicals and led to the formation of CH₃O and CH₃OO, increasing the probability of the formation of CH₃OH and HCHO. However, introducing excess CH₄ into the system favored the decomposition of CH₃OH and HCHO: CH₃OH + (CH₃, OH, H) = CH₂OH + (CH₄, H₂O, H₂), HCHO + (H, OH) = HCO + (H₂, H₂O). Figure 5(c) shows that F_{C₂} reached its maximum, 1.93 and 3.75%, at CH₄ feeding concentrations of 10% and 15% at applied powers of 50 W and 100 W, respectively.

Figure 6 shows the effect of CH₄ feeding concentration on F_{CO} and F_{CO₂}. F_{CO₂} decreased to a minimum 12.2% at a CH₄ feeding concentration of 8% and an applied power of 100 W. It declined from 27.8% to 10.5% as the CH₄ feeding concentration increased from 2 to 30% at an applied power of 50 W. The reaction pathway was possibly favored CH_x + O₂ = CO₂ + xH and CO + OH = CO₂ + H at 100 W, this increasing F_{CO₂}.

O₂ FEEDING CONCENTRATION

Figure 7 plots the influence of O₂ feeding concentration on the CH₄ conversion ratio. Increasing O radicals enhanced the reaction rate of CH₄ + O = CH₃ + OH and led to the elevation of CH₄ conversion ratio. Figure 8(a) shows that F_{CH₃OH} reached its maximum, 0.79 and 0.26%, at an O₂ feeding concentration of 8% at both 50 W and 100 W, respectively. Figure 8(b) shows that F_{HCHO} reached its maximum, 11.9 and 1.84%, at an O₂ feeding concentration of 8% at both 50 W and 100 W. Interestingly, the yields of CH₃OH and HCHO were higher at an input power of 50 W than at 100 W. A lower input power favored the formation of CH₃OH and HCHO over the decomposition of CH₃OH or HCHO to CO₂, which was favored at a higher reaction temperature. Figure 8(c) shows that F_{C₂} increased steadily from 1.20 to 1.56% as the O₂ feeding concentration increased from 1 to 8% (O₂/CH₄ = 0.13 to 1.0); it apparently decreased to 0.18% at an O₂ feeding concentration of 40% (O₂/CH₄ = 5.0) at an applied power of 50 W. Furthermore, the F_{C₂} declined from 4.35 to 0.26% as the O₂ feeding concentration increased from 1 to 40% at an applied power of 100 W. The raising O radicals were unfavorable to the formation of CH₃OH, HCHO and C₂ compounds. This was possibly due to the increasing reaction rate of CH₃OH + O = CH₂OH + OH, HCHO + O = HCO + OH, and C_xH_y + O = C_xH_{y-1} + OH.

Figure 9 plots the effect of O₂ feeding concentration on F_{CO} and F_{CO₂}. The effluent temperature at the top of the reactor was around 60° C. The selectivity shifts toward CO and CO₂ from CH₃OH as the O₂ content increases. The results are similar to those of Zhou's research (1998), which indicated that the formation of H₂ is hard to detect when the O₂ content in the feed mixture exceeds 15%, suggesting that the oxidation of CH₄ to CO₂ and H₂O is stronger at higher O₂ concentrations.

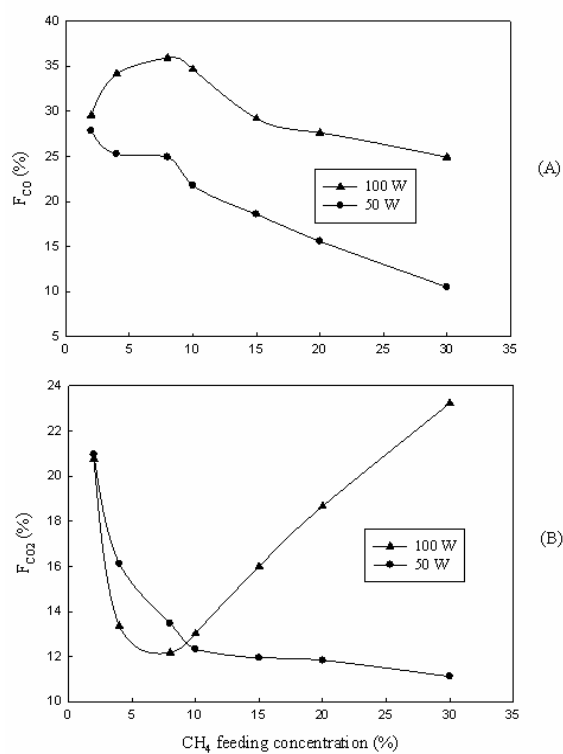


Figure 6. Influence of the CH₄ feeding concentration on (A) F_{CO} (%) (B) F_{CO₂} (%) (O₂/CH₄ = 1.0, total flow rate = 100scm).

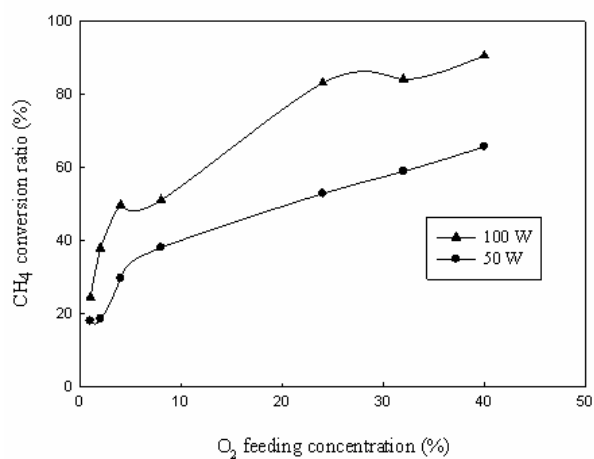


Figure 7. Influence of O₂ feeding concentration on CH₄ conversion ratio ([CH₄] = 8%, total flow rate = 100scm).

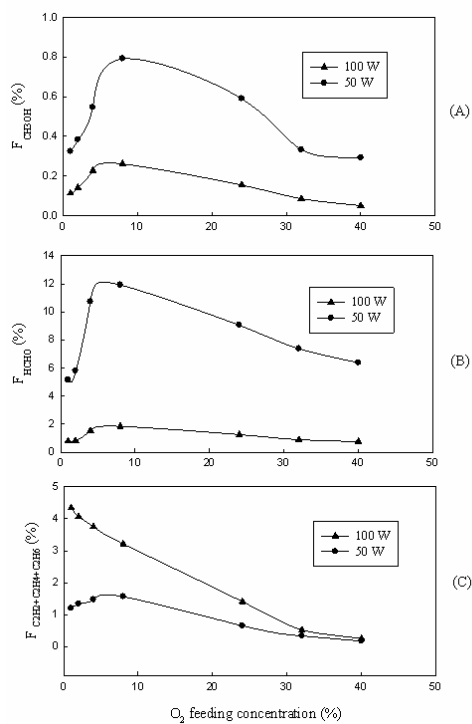


Figure 8. Influence of the O₂ feeding concentration on (A) F_{CH₃OH} (%) (B) F_{HCHO} (%) (C) F_{C₂H₂+C₂H₄+C₂H₆} (%) ([CH₄] = 8%, total flow rate = 100sccm).

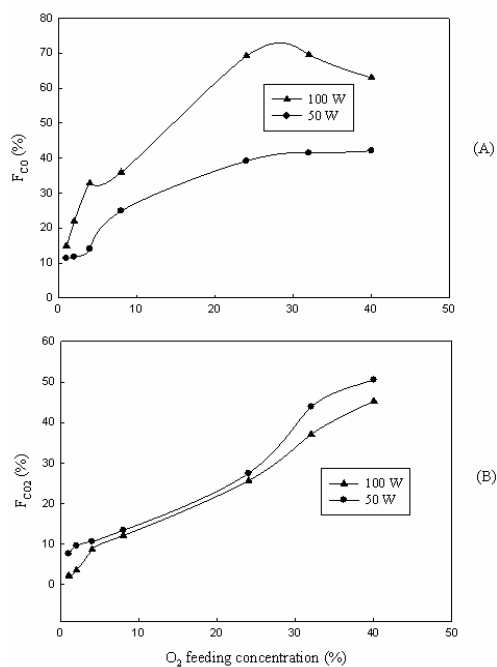


Figure 9. Influence of the O₂ feeding concentration on (A) F_{CO} (%) (B) F_{CO₂} (%) ([CH₄] = 8%, total flow rate = 100sccm).

POSSIBLE PATHWAYS OF FORMATION OF CH₃OH

Figure 10 proposes major formation pathways of CH₃OH. First, RF plasma is used to generate high-speed electrons and excited species via discharge at low pressure. These energetic species impact CH₄ and O₂ to generate free radicals, positive ions, negative ions, and excited molecules or atoms, through electron impact dissociation, electron ionization–dissociation, electron attachment and Penning dissociation processes (Chapman, 1980). Then, large numbers of free radicals, such as H, CH₃, CH₂, CH and O, were produced with small amounts of ions. The probability that CH_x radicals collide with each other to generate higher hydrocarbons was higher than that associated with the formation of CH₃O or CH₃OO radicals, because the separating plate isolates the excited radicals from CH₄ and O₂ inside the reactor. However, the effluent radicals recombine with each other or attach to O radicals in the rear part of the reactor, to form CH₃O or CH₃OO radicals and produce CH₃OH and HCHO. Consequently, further plasma diagnoses must be performed to verify the details of the reaction mechanisms.

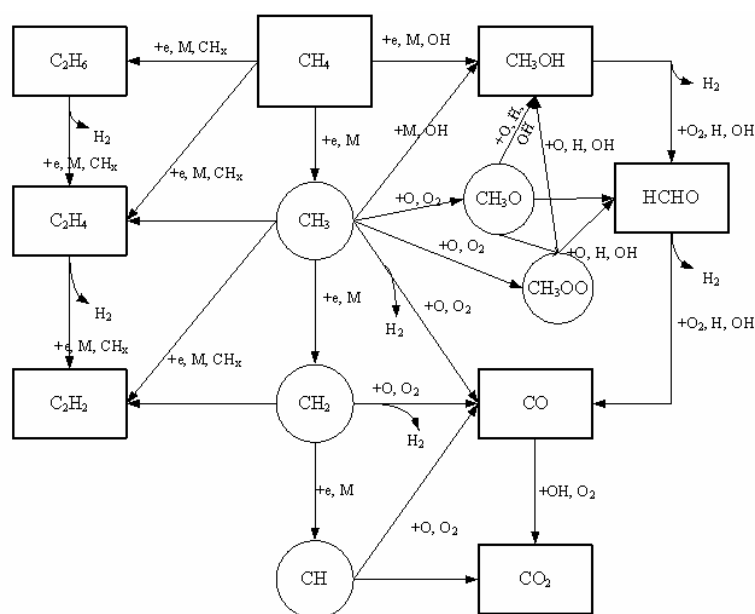


Figure 10. Proposed reaction pathways in the CH₄/O₂/Ar plasma system.

CONCLUSIONS

This work demonstrates the possibility of directly converting CH₄ into CH₃OH, HCHO, C₂H₆, C₂H₄ and C₂H₂ without adding a catalyst to the RF plasma system. Neither carbon black nor a deposit was formed during the experiment. The carbon balance in all experiments was between 0.87 and 1.24. At a

given specific energy, a higher applied power did not favor the partial oxidation of CH₄ to CH₃OH and HCHO. However, a CH₄ feeding concentration of less than 15% or an O₂ content of under 10% favored the formation of CH₃OH and HCHO. This study also addressed the conversion of methane into valuable chemicals, such as HCHO, CH₃OH, C₂H₆, C₂H₄ and C₂H₂, in the non-catalyzed RF plasma system. The one-step oxidation of methane into methanol, formaldehyde, ethane, ethylene and acetylene considerably reduces the cost of the process and constitutes an alternative method to reducing the concentration of the global warming gas, methane. Increasing the pressure and yield of CH₃OH by altering the design of the RF plasma system reactor can be explored in future research.

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