Direct Conversion of Methane into Methanol and Formaldehyde in an RF Plasma Environment I: A Preliminary Study

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ABSTRACT

The direct conversion of methane (CH_4) into methanol (CH_3OH) and HCHO in an Argon (Ar) 50W radio-frequency plasma system was applied and the effects of various feed compositions, CH_4/O_2 ratio, and plasma discharge areas were compared. Additionally, the effects of various methane to oxygen ratios and plasma discharge areas were studied. It was found that in an Ar stream, the CH_3OH conversion ratio in the CH_4/O_2 plasma system was higher than that in CH_4/CO, CO/H_2 and $CH_4/H_2/O_2$ plasma systems. The conversion of CH_4 reached 19.1% at CH_4/O_2 = 40/60; the yield of CH_3OH was 1.12% and 16.0% CO, the major product, was produced. A larger plasma discharge area, resulting in a longer residence time, corresponded to higher CH_4 conversion, but a lower CH_3OH conversion ratio, because of further decomposition into CO and CO_2. Interestingly, no carbon deposition was observed in the RF plasma system, and the carbon balance was between 0.94 and 1.19.

Keywords: Methane, methanol, formaldehyde, radio-frequency plasma

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INTRODUCTION

Methane (CH_4) is a major contributor to the human-caused greenhouse effect. Much attention has been paid to the conversion of methane into higher hydrocarbons and easily transportable liquids, such as methanol (CH_3OH) and formaldehyde (HCHO). It is expected that methane will become increasingly important in the production of energy and chemicals during this century (Roth, 1994; Brown and Parkyns, 1991). Of all available direct conversion processes, the partial oxidation of methane into useful oxygenates has great potential and is considered to be one of the greatest challenges for catalysis (Gesser, et al. 1985; Crabtree, 1985; Krylov, 1993).

Direct conversion technology could significantly impact the realization of more efficient energy, conserving resources and protecting the atmosphere by reducing the concentration of exhausted greenhouse gas. The difficulty in the direct conversion of methane, both catalytically and thermally, concerns the high stability of the C-H bond in the methane molecule, which exceeds that in all other hydrocarbons (Lunsford, 2000). Catalytic methods of methane conversion must eliminate the need for high reaction temperatures and the poisoning of catalysts (Lodeng et al., 1995). Accordingly, the direct synthesis of methanol from methane can support a new synthetic process that consumes much less energy.

Nonthermal plasma has been used recently to excite small, stable molecules, using energetic electrons and no heating of gases. Energetic electrons are generated using either a corona, a pulse discharge, a microwave discharge, or a dielectric-barrier discharge (Suib et al. 1993; Liu et al. 1999; Huang et al. 2000). The products of methane conversion obtained using nonthermal plasma are mainly ethylene, acetylene, hydrogen, carbon monoxide, carbon dioxide, and some oxygenates. Some of results have led to the formation of carbon black and plasma polymerized carbon film. Very few studies have used a radio-frequency (RF) plasma system to examine the direct conversion of methane into a useful liquid fuel. In this work, the direct conversion of methane into methanol in an RF plasma system was applied and the effects of various feed compositions were compared. Additionally, the effects of various methane to oxygen ratios and plasma discharge areas were studied.

METHODS

Figure 1 illustrates the RF plasma reactor used and schematically depicts the experiment’s setup. Reactants CH_4/CO/Ar, CO/H_2/Ar, CH_4/O_2/Ar, and CH_4/O_2/H_2/Ar were metered using Brooks Type 5850E mass flow controllers at a total flow of 100 $cm^3.min^{-1}$. They were then separately introduced into the reactor (4.5 cm I.D. $\times$ 15 cm height). The inside of the reactor was separated into two sections by a

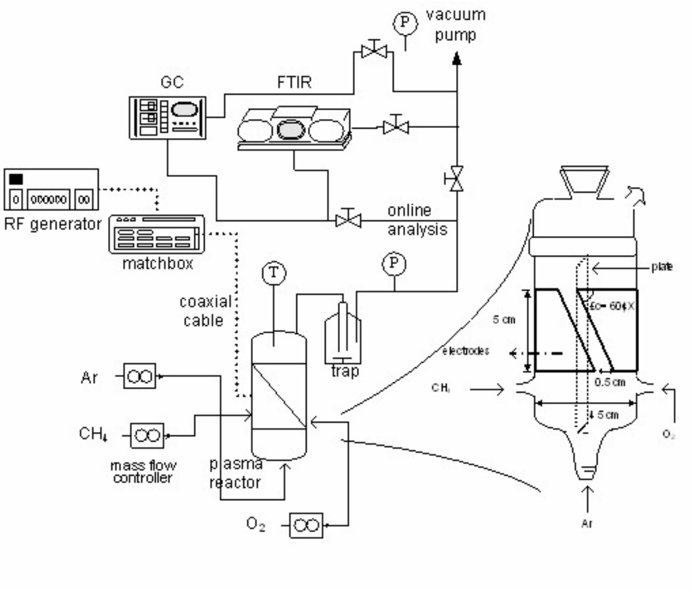

Fig 1. Sketch of the RF plasma system

glass plate to dissociate the input gases individually and then recombine them in the effluent of the reactor. This particular reactor design was intended to improve the possibility of recombining free radicals and prevent the decomposition of CH_3OH in the reactor once it was formed. A plasma generator (PFG 600 RF, Fritz Huttinger Elektronik Gmbh) at 13.56 MHz, with a matching unit (Matchbox PFM), produced the RF plasma discharge. The pressure of the system had to be adjusted to under 0.0013 mbar before the experiments were performed to eliminate background contamination. Reactants and final products were first identified by gas chromatography (HP5890A); then all species were identified and their concentrations quantified using an on-line Fourier Transform Infrared (FTIR) Spectrometer (Thermo Nicolet AVATRA 360).

FTIR quantification data were obtained through a carbon balance to evaluate the significance of both deposition and condensation in the sampling and analyzing apparatus.

$$CB = \frac{\sum_{i=1}^{n} [(C_{out})_i \times (N_i)]}{[CH_4]_f}$$

CH_4 was partially oxidized at 13.3 mbar and 50W. The conversion of CH_4 (X_{CH4}) and fraction of total input carbon converted into CH_3OH (F_{CH3OH}), HCHO (F_{HCHO}) and C_2H_2 + C_2H_4 + C_2H_6 (F_{C2}) were calculated as,

$$X_{CH4} = \frac{[CH_4]_c}{[CH_4]_f} \times 100\% \quad (1)$$

$$F_{CH3OH} = \frac{[CH_3OH]_p}{[CH_4]_f} \times 100\% \tag{2}$$

$$F_{HCHO} = \frac{[HCHO]_p}{[CH_4]_f} \times 100\% \tag{3}$$

$$F_{C2} = \frac{[C_2H_2 + C_2H_4 + C_2H_6]_p \times 2}{[CH_4]_f} \times 100\% \tag{4}$$

$(C_{out})_i$ is the concentration of species i in the effluent (%)
N_i is the number of carbon atoms in the chemical formula for species i in the effluent
n is the total number of species in the effluent
$[CH_4]_f$ is the CH_4 feeding concentration (%)
$[CH_4]_c$ is the amount of CH_4 consumed (%)
$[CH_3OH]_p$ is the amount of CH_3OH produced (%)
$[HCHO]_p$ is the amount of HCHO produced (%)
$[C_2H_2 + C_2H_4 + C_2H_6]_p$ is the amount of $C_2H_2 + C_2H_4 + C_2H_6$ produced (%).

RESULTS AND DISCUSSION

SYNTHESIS OF METHANOL AND FORMALDEHYDE FOR VARIOUS FEED COMPOSITIONS

Table 1 shows X_{CH4}, F_{CH3OH}, F_{HCHO} and by-products in various RF plasma systems (CH_4/CO/Ar, CO/H_2/Ar, CH_4/O_2/Ar, and $CH_4/O_2/H_2$/Ar), as well as the ratio of the various reactants. The experimental conditions were: 50W applied power; 13.3 mbar operational pressure, and 100 $cm^3.min^{-1}$ total flow. The combination of reactants affects the patterns of the by-products in the effluent. X_{CH4} was present in the least amount and no CH_3OH or HCHO was formed in the CO/H_2/Ar system. Only CO_2, CH_4 and H_2O were produced in the CO/H_2/Ar system. In contrast, more by-products—CO, CO_2, CH_3OH, HCHO, C_2H_2, C_2H_4, C_2H_6, H_2O and H_2—were detected in the CH_4/CO/Ar and CH_4/O_2/Ar system. Interestingly, neither HCHO, nor hydrocarbons were detected in the $CH_4/O_2/H_2$/Ar system. F_{CH3OH} was the most present (0.96%) in the CH_4/O_2/Ar system, with a CH_4/O_2 ratio of 30/60. Increasing the CH_4/O_2 ratio to 30/7 reduced the F_{CH3OH} in all except the CH_4/CO/Ar system. Based on these results, the CH_4/O_2/Ar combination was chosen in the following experiment.

Table 1. The reaction combination of different reactants.

	$CH_4/CO/Ar$		$CO/H_2/Ar$		$CH_4/O_2/Ar$		$CH_4/O_2/H_2/Ar$	
ratio	30/60/10	30/7/63	30/60/10	30/7/63	30/60/10	30/7/63	30/30/30/10	30/7/7/46
X_{CH4}(%)	15.2	11.3	3.55	5.04	20.9	14.3	26.6	17.2
F_{CH3OH}(%)	0.05	0.07	0.00	0.00	0.96	0.14	0.50	0.07
By-products	CO_2, CH_3OH, HCHO, C_2H_2, C_2H_4, C_2H_6, H_2, H_2O		CH_4 、CO_2		CO_2, CO, CH_3OH, HCHO, C_2H_2, C_2H_4, C_2H_6, H_2, H_2O		CO_2, CO, CH_3OH, H_2O	

METHANOL AND FORMALDEHYDE SYNTHESIS WITH VARIOUS CH_4 TO O_2 RATIOS

Table 2 presents the effect of a CH_4/O_2 feeding concentration on the conversion of CH_4. Pure CH_4 has typically been regarded as rather chemically inactive, but easily decomposes in the RF plasma system. Unlike in other studies (Matsumoto, et al. 2001), X_{CH4} was less than 12% at a 2% CH_4 feeding concentration, and a 50 cm^3/min^{-1} total flow rate, while X_{CH4} was about 4% with a 5.0 mL/min^{-1} CH_4 flow rate (Taylor et al. 2000). X_{CH4} with typical solid catalysts reported by Otsuka (2001) was 0.7% to 18.5%. In the RF system, applying 50W yielded 14.8 to 38.1% CH_4 conversion, while in the DBD system, 100W of input power yielded 5.97% CH_4 conversion (Jiang et al. 2002). Matsumoto (2001) stated that the intensities in Ar excitation drastically declined upon the introduction of a feeding concentration of CH_4 of only 2% into the Ar stream, and their system exhibited a large energy transfer from excited Ar species to reactant molecules. This suggestion was extended to the RF system. X_{CH4} was higher in the RF plasma system with Ar inflow (CH_4/O_2 at 30/60 and 50/40) than in that without (CH_4/O_2 = 40/60, 50/50).

The highest F_{CH3OH}, F_{HCHO} and F_{C2} were 1.12, 11.9 and 1.56% with CH_4/O_2 ratios equaling 40/60, 8/8 and 8/8, respectively. The highest F_{CO} and F_{CO2} were 24.9 and 23.1% with CH_4/O_2 ratios of 8/8 and 50/50, respectively. Interestingly, F_{C2} generally decreased as the CH_4 and O_2 feeding concentrations increased. No carbon deposition occurred in the Matsumoto et al. RF system, and the carbon balance was 0.97 to 1.19.

Table 2. The effect of CH_4 to O_2 ratio on CH_4 conversion.

CH_4/O_2 ratio	X_{CH4}(%)	F_{CO}(%)	F_{CO2}(%)	F_{CH3OH}(%)	F_{HCOH}(%)	F_{C2}(%)	Carbon balance
8/8	38.1	24.9	13.4	0.79	11.9	1.56	1.14
30/60	20.9	16.4	7.20	0.96	0.24	0.33	1.04
40/60	19.1	16.0	6.38	1.12	0.18	0.28	1.05
50/40	19.3	11.2	3.04	0.90	0.80	0.24	0.97
50/50	14.8	8.71	23.10	0.15	1.91	0.02	1.19

METHANOL AND FORMALDEHYDE SYNTHESIS FOR VARIOUS PLASMA DISCHARGE AREAS

Table 3 shows the effect of the plasma discharge area on CH_4 conversion. Experimental conditions were $[CH_4]_{in}$ = 8%, $[O_2]_{in}$ = 8%, applied power = 50 W and operational pressure = 13.3 mbar. Increasing the discharge area increased the residence time thus increasing X_{CH4}. Increasing the discharge area reduced F_{CH3OH} and F_{C2}, while F_{HCHO} initially increased but then fell. F_{CO} and F_{CO2}, meanwhile, increased with increased discharge area. A longer residence time favored the formation of CO and CO_2 as final products of the dominant reaction pathway (Matsumoto et al. 2001). CH_3OH is oxidized into HCHO and further decomposed into CO and CO_2 when the residence time is increased. Therefore, a smaller discharge area favors the production of CH_3OH.

Direct conversion of methane into methanol in the RF plasma system was shown to be possible, indicating a potential for extensive abatement and reuse of methane. Experiments were conducted to clarify the influence of feed composition on CH_3OH formation, on CH_4/O_2 ratio and on the plasma discharge area. Experimental results revealed that the combination $CH_4/O_2/Ar$ system favors a better CH_3OH conversion fraction. The by-products detected in the $CH_4/O_2/Ar$ plasma system were CO, CO_2, CH_3OH, HCHO, C_2H_2, C_2H_4, C_2H_6, H_2O and H_2. For various CH_4/O_2 ratios, the highest F_{CH3OH}, F_{HCHO} and F_{C2} were 1.12, 11.9 and 1.56% with CH_4/O_2 ratios of 40/60, 8/8 and 8/8, respectively. The highest F_{CO} and F_{CO2} were 24.9 and 23.1% with CH_4/O_2 ratios of 8/8 and 50/50, respectively. Moreover, a larger plasma discharge area, resulting in a longer residence time, led to higher CH_4 conversion, but a lower CH_3OH conversion ratio, owing to further decomposition into CO and CO_2. Therefore, the $CH_4/O_2/Ar$ plasma system of reactor A was selected as the basis for the further investigation of the effects of experimental parameters on X_{CH4}, F_{CH3OH} and F_{HCHO}.

Table 3. The effect of plasma discharge area on CH_4 conversion.

Discharge area (cm^3)	X_{CH4}(%)	F_{CO}(%)	F_{CO2}(%)	F_{CH3OH}(%)	F_{HCOH}(%)	F_{C2}(%)	Carbon balance
A (320)	38.1	24.9	13.4	0.79	11.9	1.56	1.14
B (450)	65.2	31.6	26.2	0.42	15.3	1.47	1.10
C (1080)	88.6	35.3	38.6	0.43	6.60	1.39	0.94

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