Oxidative Coupling and Reforming of Methane with Carbon Dioxide Using a Pulsed Microwave Plasma under Atmospheric Pressure

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A conventional high voltage wire-like plasma enhanced and spread by a pulsed microwave was used to study the oxidative coupling and reforming of CH_4 with CO_2 to CO, C_2H_2, C_2H_4, and H_2. Under the conditions of atmospheric pressure, a flow rate of 200 mL/min ($CH_4/CO_2 = 1.5:1$), peak microwave power of 120 W, and a pulse duty factor of 100/100 ms, conversions of CH_4 and CO_2 were 70.8% and 68.8%, respectively; selectivities to CO, C_2H_2, and C_2H_4 were, respectively, 75%, 17.8%, and 4.1%, and there was no carbon deposit. The ratio of H_2/CO increased with increasing CH_4 concentration in the feed gas, and a H_2/CO ratio of 2 could be obtained at a ratio 2:1 of CH_4 to CO_2, which is acceptable for Fischer-Tropsch and other synthesis processes. The energy efficiency of the pulsed microwave plasma was obviously improved. We suggested that this enhanced pulsed plasma is useful for oxidative coupling and reforming of CH_4 with CO_2 in C1 Chemistry.

1. Introduction

Methane and carbon dioxide are two major greenhouse gases, and carbon dioxide is present in many natural gas resources. Oxidative coupling and selective oxidation of methane to produce ethylene and higher hydrocarbon have received worldwide attention as a potentially interesting process for upgrading natural gas since 1982.[1] Oxidative coupling of methane to ethane[2] and ethylene[3] requires a higher reaction temperature and higher pressure due to the similar high dissociation energy of activation of most C−H bonds. The most important reactions involving CO_2 are as follow:[4,5] (1) the incorporation of CO_2 into the C−C, C−H, and C−N bonds with formation of carboxy and carbonyl compounds; (2) the oxidation of other hydrocarbons using CO_2 as an oxidant. However, there are some difficulties in conventional catalytic conversion of CO_2. The principal difficulty is from the intensive energy consumption and the expensive hydrogen source.[6] Due to its high H−C ratio, methane is a very good co-reactant for CO_2 utilization. Most of these research interests focus on synthesis gas ($CO + H_2$) formation from CH_4 and CO_2 via reaction 1:[7−16]

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta G_{1073K} = -254 \text{ KJ/mol} \quad (1)$$

Such a reaction was first described by Fischer and Tropsch using various catalysts such as Ni supported on silica at 860 °C.[17] The high reaction temperature implied that this process is very costly.[18] On the other hand, the undesirable carbon deposits are not avoidable with the present catalyst design in CO_2 reforming of CH_4.

As an effective approach, plasma technology has been applied to the conversion of CH_4 and CO_2. Larkin et al. studied the oxidative coupling of methane with carbon dioxide using an arc dielectric-barrier plasma reactor. The selectivities of oxygenates (methanol, formaldehyde, formic acid, methyl formate) amount to 50−65%.[19] Zhou et al. studied methane reforming with carbon dioxide using a high-frequency AC nonthermal plasma. They found that most of the methane can be converted to carbon monoxide and hydrogen.[20] Huang et al. found that methane reforming with carbon dioxide using an AC arc plasma has a higher energy efficiency than using an AC glow plasma.[21] Yao and co-workers reported the

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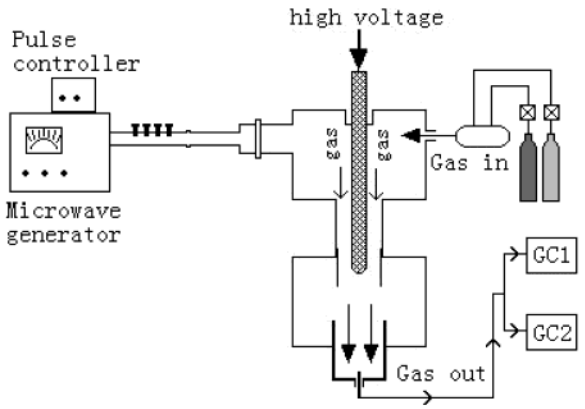

Figure 1. Schematic diagram of the experimental setup.

oxidative coupling and reforming of CH_4 with CO_2, using a high-frequency pulsed plasma, and have achieved a high energy efficiency.[22,23] For oxidative coupling of methane using the microwave plasma with or without catalysts, some results at lower work pressure (23∼50 Torr) have been reported.[24] But the oxidative coupling and reforming of CH_4 with CO_2 using pulsed microwave plasma at atmospheric pressure is relatively unexplored, which is probably due to difficulty in obtaining a low-temperature microwave plasma at atmospheric pressure.

Through a compatibility study of conventional high-voltage wire-like plasma and microwave cavity, a conventional wire-like plasma enhanced and spread by pulsed MW was chosen.[25] On one hand, the microwave can spread a wire-like plasma to form an umbrella-like plasma, whose area (or volume) is much expanded and the activation of plasma is enhanced; on the other hand, it inhibits abrupt transition of microwave discharge from deficient density to excessive density, which helps sustain a low-temperature nonequilibrium plasma. A plasma chemical reaction apparatus was manufactured in which high voltage discharged wire-like plasma was enhanced by pulsed microwave, and a low-temperature (about 500 °C, see ref 26) nonequilibrium microwave plasma was achieved at atmospheric pressure. Using this device, the oxidative coupling and reforming of CH_4 with CO_2 at atmospheric pressure was investigated. The conversions, selectivities, and energy efficiencies were reported.

2. Experimental Section

The experiment setup is schematically shown in Figure 1. The flow rate of feed gas was measured by a D07 mass flow controller and a D08 display unit (Beijing Jianzhong Machinery Factory), which were calibrated by a soap film meter. The frequency of the MW generator is 2450 MHz, with a maximum output power of 600 W and a pulse duration between 10 and 999 ms which is continuously adjustable. The pulsed MW plasma reactor was composed mainly of a coupling cavity, a coaxial line, and a resonance cavity. The high voltage is applied to the internal conductor to form a wire-like plasma between the internal conductor and inner walls of the outer conductor. When pulsed microwave is introduced into the cavity, the wire-like plasma is enhanced and spread to form an umbrella-like plasma, which is continuously distributed in space. A short quartz tube with i.d. of 20 millimeter, that is attached to the end of the coaxial conductors, can be used to force the feed gas to flow across the plasma zone.

A mixture of methane and carbon dioxide was introduced into the coupling cavity and flowed through the plasma zone. Carbon compounds in the products from the exit of the reactor were analyzed with an online gas chromatograph (GC950, Shanghai Institute of computing-technique; TCD) equipped with a 2 m Porapak Q. Concentrations of H_2 and argon (internal standard gas for calculation of the carbon balance) were measured with another online gas chromatograph (GC920, Shanghai Institute of computing-technique; TCD) equipped with a 2 m TDX-01. All experiments were carried out at atmospheric pressure.

The overall conversions were defined as

$$\mathrm{CH_4\ conversion} = [(\text{moles of } CH_4 \text{ before reaction}) - (\text{moles of } CH_4 \text{ after reaction})]/(\text{moles of } CH_4 \text{ before reaction}) \times 100\%$$

$$\mathrm{CO_2\ conversion} = [(\text{moles of } CO_2 \text{ before reaction}) - (\text{moles of } CO_2 \text{ after reaction})]/(\text{moles of } CO_2 \text{ before reaction}) \times 100\%$$

Selectivity to CO was defined as

$$\mathrm{CO\ selectivity} = (\text{moles of CO produced})/[(\text{moles of } CH_4 \text{ converted}) + (\text{moles of } CO_2 \text{ converted})] \times 100\%$$

Selectivity to C_2H_2 or C_2H_4 was defined as

$$C_2H_2 \text{ or } C_2H_4 \text{ selectivity} = (2 \times \text{moles of } C_2H_2 \text{ or } C_2H_4 \text{ produced})/[(\text{moles of } CH_4 \text{ converted}) + (\text{moles of } CO_2 \text{ converted})] \times 100\%$$

The input power for wire-like discharge is 5 W, and the peak power of microwave is between 80 and 160 W in our experiments. The pulse duration is represented with milliseconds.

The conversion ability of atmospheric pulsed microwave plasma is given (in mole of $(CH_4 + CO_2)_{(\text{converted})}/J_{(\text{plasma power})}$) as

$$\text{conversion ability} = (\text{moles of } CH_4 \text{ and } CO_2 \text{ converted during one minute})/60P$$

which can represent the energy efficiency of the pulsed microwave plasma.

3. Results and Discussion

3.1. Influence of Pulse Frequency. We first investigated the influence of pulse frequency at a CH_4/CO_2 ratio of 3/2. The pulse duty factor was set at 1/1, with increasing of pulse duration from 50 to 500 ms, the pulse frequency decreased from 10 PPS to 1 PPS. Conversions of CH_4 and CO_2 decreased with increasing pulse duration from 50 to 350 ms, and there were the minimal values at the pulse duration of 350 ms, which was shown in Figure 2. CH_4 conversion was higher than CO_2 conversion, as there are some CO_2 formation reactions:

$$OH + CO = H + CO_2 \quad (2)$$

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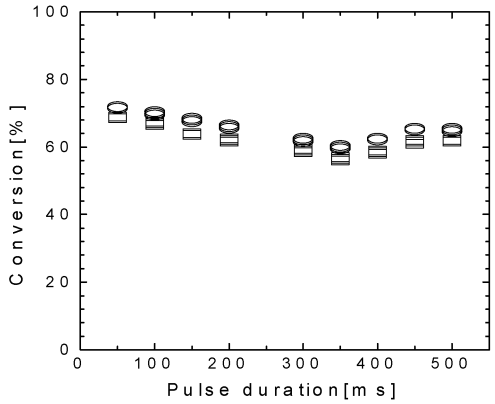

Figure 2. Influence of pulse duration on methane (○) and carbon dioxide (□) conversions. CH_4/CO_2 = 1.5:1, pulse duty factor = 1:1, peak power of MW = 120 W, feed flow rate = 200 mL/min.

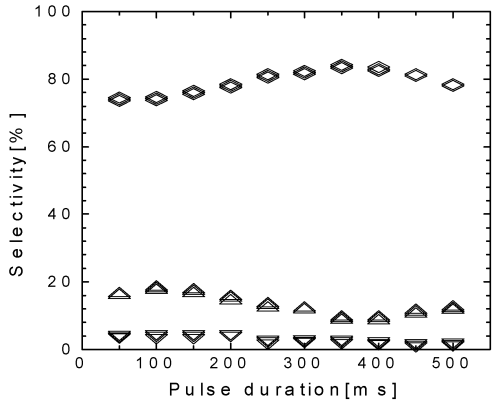

Figure 3. Selectivities of CO (◇), C_2H_2 (△), and C_2H_4 (▽) at various pulse durations. CH_4/CO_2 = 1.5:1, pulse duty factor = 1:1, peak power of MW = 120 W, feed flow rate = 200 mL/min.

The minimal values of conversions came from the dimension of reactor and the feed flow rate. The i.d. of the coaxial line and quartz tube is 20 mm; when the flow rate of feed gas passing across the plasma is 200 mL/min, the linear gas velocity is 10.6 mm/s. Viewed from the side, the thickness of the umbrella-like plasma zone in the experiments is about 5 mm, so the residence time of feed gas in the plasma zone is about 470 ms. Considering the factor that abrupt volume expansion of feed gas in the pulsed MW plasma would result in a backflow toward the plasma zone, the time in which the unit mass of feed gas passing through the plasma zone is longer than 470 ms. With a pulse duty factor of 1/1, when the pulse duration is longer (e.g., 300, 350, and 400 ms), a part of the feed gas would flow across the plasma zone without being activated during the intermission of plasma, which results in the decrease of conversions. When the pulse duration is short (e.g., 100 and 200 ms), a unit mass of feed gas flowing across the plasma could experience 2−3 pulses of time of MW plasma although single pulse duration is shorter, so the conversions could also reach a high value.

In the products, there is only a spot of steam (H_2O) produced (eq12) and no oxygen observed, so the H_2O was ignored in the analysis.

The selectivity to CO increased with the increase in the pulse duration, but selectivity to C_2H_2 and C_2H_4 decreased (Figure 3). This implied the rapid quenching

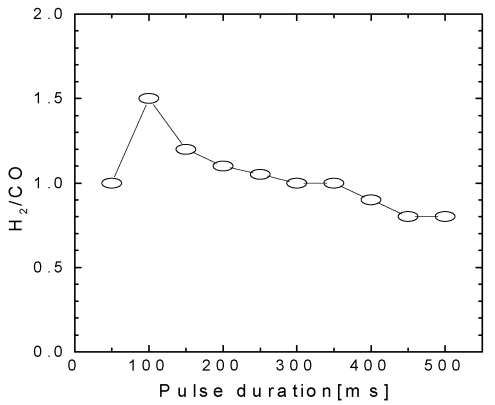

Figure 4. Ratios of H_2/CO at various pulse durations. Conditions are the same as those in Figure 3.

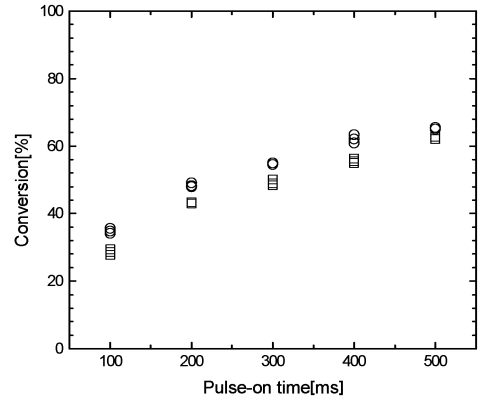

Figure 5. Influence of pulse-on time on methane (○) and carbon dioxide (□) conversions. CH_4/CO_2 = 1.5:1, pulse intermission = 500 ms, peak power of MW = 120 W, feed flow rate = 20 mL/min.

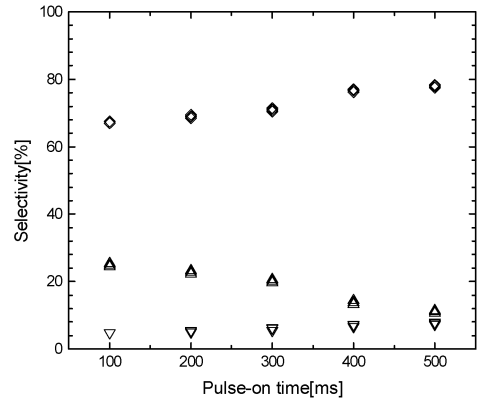

Figure 6. Selectivities of CO (◇), C_2H_2 (△), and C_2H_4 (▽) at various pulse-on times. Conditions are the same as those in Figure 5.

of effluent was important for the formation of C_2H_2. But it is still unknown why there is no trace of C_2H_6 in the products. The ratio of H_2/CO in the product is shown in Figure 4. The H_2/CO ratio peaked at a pulse duration of 150 ms. The H_2/CO ratio was lower than 1.0 when pulse duration exceeded 400 ms.

3.2. Influence of Pulse-on Time. For investigating the enhancement effect of pulsed microwave, we studied the influence of changing the pulse-on time. In the experiments, the pulse intermission of microwave was set at 500 ms, the pulse-on time increased from 100 to 500 ms. Conversions of CH_4 and CO_2 at various pulse

durations are shown in Figure 5. Conversions of CH_4 and CO_2 increased remarkably when the pulse-on time increased. The increases in conversion of CH_4 and CO_2 were obviously due to the increase in input power. The selectivity to each product is shown in Figure 6. The selectivity to CO increased and that of C_2H_2 decreased as the pulse-on time increased. The selectivity to C_2H_4 did not change significantly. It was found, that in a plasma process, the most important reactions for CH_4 consumption are the electron-impact dissociation to radicals CH_x (x = 0,1,2,3), as was already pointed out by Oumghar et al.[27] and Shigeru et al.:[28]

$$e\ (\epsilon > 10\ eV) + CH_4 \rightarrow CH_4(S_1,S_2) + e \quad (3)$$

$$CH_4(S_1,S_2) \rightarrow CH_3 + H \quad (4)$$

$$CH_3 \rightarrow CH_2 + H \quad (5)$$

$$CH_2 \rightarrow CH + H \quad (6)$$

$$CH \rightarrow C + H \quad (7)$$

CO_2 can be dissociated to produce reactive species including O, oxygen anion in plasma reaction:[4,29]

$$CO_2 \rightarrow CO + O \quad (8)$$

C_2H_2 and C_2H_4 are mainly formed via the recombination of radicals. Expect for the dissociation of carbon dioxide, reactive oxygen species could result in formation of CO via reactions:[29]

$$CH_3 + O \rightarrow HCHO + H \quad (9)$$

$$HCHO + O \rightarrow OH + CHO \quad (10)$$

$$CHO + O \rightarrow OH + CO \quad (11)$$

$$OH + O \rightarrow H_2O \quad (12)$$

$$H_2O + O \rightarrow OH + OH \quad (13)$$

$$CHO + H \rightarrow CO + H_2 \quad (14)$$

The change of CO and C_2H_2 selectivities with pulse-on time (namely, the residence time of feed gas in the plasma zone) indicated that the rapid quenching of plasma favors the production of acetylene.

3.3. Influence of CH_4 Concentration in Feed Gas. The main products are CO and H_2 in methane coupling and reforming with carbon dioxide using pulsed microwave plasma. The synthesis gas ($CO + H_2$) is mainly used to produce liquid fuels and other chemicals via the Fischer−Tropsch reaction, and to produce CH_3OH via the following reactions:

$$CO + 2H_2 \rightarrow (-CH_2-)_n + H_2O \quad (15)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (16)$$

The dry reforming of CH_4 with CO_2 is usually carried out at a ratio 1:1 of CH_4 to CO_2, yielding a 1:1 mixture of H_2 and CO (eq 17):

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (17)$$

Since the synthesis gas from dry reforming of CH_4 (eq 16) cannot be directly used for Fischer−Tropsch reaction and CH_3OH production, the reaction yielding a high H_2/CO is required. We then carried out CH_4 reforming with CO_2 at various ratios of CH_4 to CO_2 and at a fixed total flow rate of 200 mL/min, the pulse duty factor was set at 100 ms/100 ms, and the peak power of microwave was 120 W. The H_2/CO ratio increased remarkably with increasing CH_4 concentration in the feed gas (Figure 7). A H_2/CO ratio of 2 could be obtained at a ratio 2:1 of CH_4 to CO_2.

The conversions of CH_4 and CO_2 at various ratios of CH_4 to CO_2 are shown in Figure 8. Conversions of both CH_4 and CO_2 decreased with increasing CH_4 concentration. Although conversions of CH_4 and CO_2 were highest at 0.5 ratio of CH_4 to CO_2, the plasma would ablate the internal conductor after a long time, which could influence the stability of plasma. Conversions of both CH_4 and CO_2 could kept around 60∼70% at a ratio of CH_4 to CO_2 from 1.5:1 to 2:1. This satisfied the next process of synthesis gas since a H_2/CO ratio of 1.5 to 2 could be given. The selectivity to each product is illustrated in Figure 9. Selectivity to CO decreased, but that of C_2H_2 and C_2H_4 increased with increasing the ratio of CH_4 to

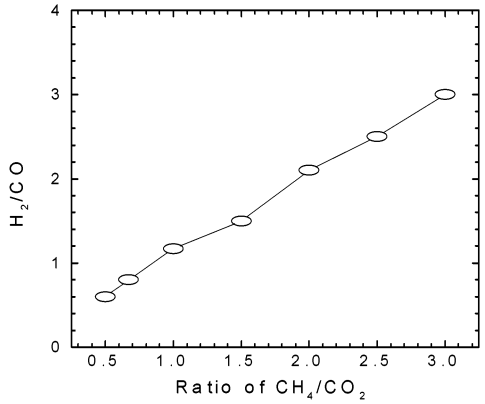

Figure 7. Ratios of H_2/CO at various ratios of CH_4/CO_2. Pulse duty factor = 100/100 ms, peak power of MW = 120 W, feed flow rate = 200 mL/min.

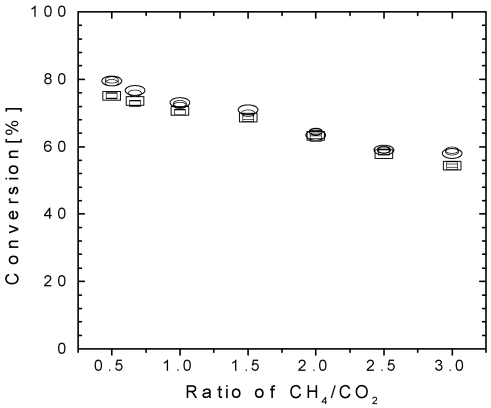

Figure 8. Influence of CH_4/CO_2 ratio on methane (○) and carbon dioxide (□) conversions. Pulse duty factor = 100/100 ms, peak power of MW = 120 W, feed flow rate = 200 mL/min.

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Table 1. Comparison of Conversion Ability to Other Plasmas

plasma	feed	flow (mL/min)	pressure (Torr)	*P* (W)	*T* (°C)	CH conversion (%)	selectivity (%) C_2H_2	C_2H_4	CO	CH_3OH	conversion ability (μ mol/J)	ref
microwave	CH_4	100	23	80		26	24	23.5			0.22	24
microwave/ catalyst	CH_4	500	50	80		8	23.5	0			0.34	24
silent	$CH_4 + O_2$	27.5	760	8	110	2.5		7.1	21.3	20	0.059	32
silent	$CH_4 + O_2/C_2H_6$	430	760	118	28	CH_4, 31.8 C_2H_6, 20 O_2, 33			18[a]	36[b]	0.37	30
pulsed AC	$CH_4 + O_2$/Ar	190	760	21	room	17		16[c]	54	24	0.36	31
dielectric-barrier	$CH_4 + CO_2$	500	760	500	80	CH_4, 40 CO_2, 20			88.5		0.18	20
AC arc[d]	$CH_4 + CO_2$	75	760	30		CH_4, 88.9 CO_2, 53.2	11.2	2.26	81.5		0.15	21
pulsed 3050PPS	$CH_4 + CO_2$	100	760	29.5	room	CH_4, 26.7 CO_2, 17.2		61.6	19.8		0.58	22
pulsed 2920PPS	$CH_4 + CO_2$	100	760	30.6	500	CH_4, 31.8 CO_2, 23.9		63.7	22.1		0.68	22
pulsed microwave plasma	$CH_4 + CO_2$	200	760	65	500	CH_4, 70.8 CO_2, 68.8	17.8	4.1	75		1.56	this study

[a] ($CO + CO_2$). [b] ($CH_3OH + HCOH + HCOOH + C_2H_5OH + HCOOCH_3$). [c] ($C_2H_4 + C_2H_6$). [d] CH_4 and CO_2 (5/5) both excited; maximum energy efficiency.

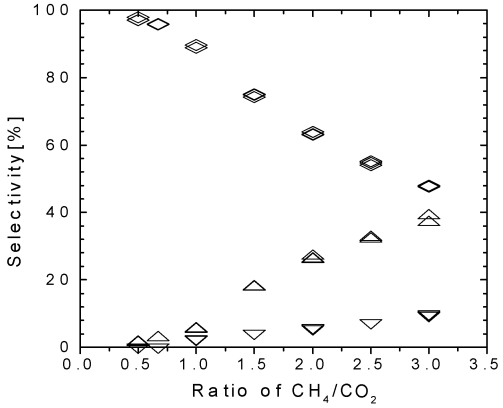

Figure 9. Selectivities of CO (◇), C_2H_2 (△), and C_2H_4 (▽) at various ratios of CH_4/CO_2. Conditions are the same as those in Figure 8.

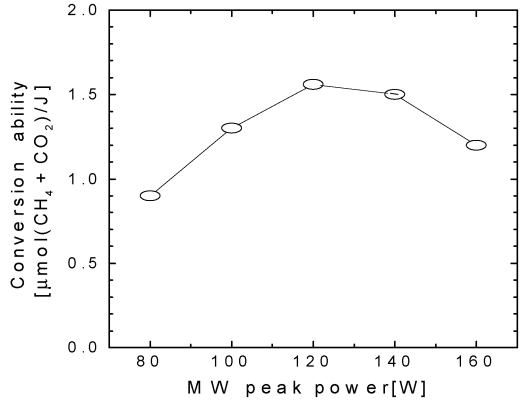

Figure 10. Conversion ability of CH_4 and CO_2 at various microwave peak powers. CH_4/CO_2 = 1.5:1, pulse duty factor = 100/100 ms, feed flow rate = 200 mL/min

CO_2. It must be mentioned that there appeared black polymer films on the inner wall of quartz tube when the ratio of CH_4 to CO_2 was more than 2.5:1. This indicated that the reactive oxygen from CO_2 dissociation plays an important role in inhibiting exorbitant dehydrogenation of methane and polymerization of methyl radicals. Since C_2H_2 and C_2H_4 are both important raw materials and H_2 is a clean energy source, this indicated that we could get these important chemicals by adjusting the ratio of CH_4 to CO_2.

3.4. Energy Efficiency of Pulsed Microwave Plasma. Almost all of the plasma experiments indicated that the energy required by the process is the highest in comparison with the others, such as a thermal chemical process. The energy efficiency of a pulsed microwave plasma is represented by a conversion ability of CH_4 and CO_2, and the energy efficiency at various microwave peak powers are shown in Figure 10. Under a fixed flow rate of 200 mL/min (CH_4/CO_2 = 1.5/1) and pulse duty factor of 100 ms/100 ms, the energy efficiency peaked at 120 W of microwave peak power. This indicated that the energy efficiency can be improved by increasing the input microwave power, but there is an upper limit at a fixed flow rate.

A comparison of our results with others using low-temperature plasma methods reported by Larkin,[30] Omumoto,[31] Shepelev,[32] Suib,[24] Zhou,[20] and Yao[22] is given in Table 1. The energy efficiency using this pulsed microwave plasma is better than that using other plasma technologies, including silent, dielectric-barrier discharges, and high-frequency pulsed plasma, and is also better than other microwave plasma with or without catalysts.

The selectivity to CO could reach as high as 97% when the ratio of CH_4 to CO_2 is 1:2 using this pulsed microwave plasma under atmospheric pressure; the selectivities of acetylene and ethylene decreased with the increase of CO_2 concentration in the feedstock.

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These facts indicate that the selectivity to each product can be adjusted easily according to the demand of subsequent chemical synthesis. So this kind of pulsed microwave plasma can believingly promote the application of plasma technologies for methane and carbon dioxide conversions.

4. Conclusions

This study demonstrates the following:

(1) The pulsed microwave under atmospheric pressure is an effective method for oxidative coupling and reforming of CH_4 and CO_2.

(2) Under a condition of 1.5:1 volume ratio of CH_4 to CO_2, total flow rate of 200 mL/min, microwave peak power of 120 W and pulse duty factor of 100 ms/100 ms, single pass conversions of CH_4 and CO_2 were around 70% and 68%, selectivities of CO, C_2H_2, and C_2H_4, H_2/CO ratio were, respectively, 75%, 17.8%, 4.1%, and 1.5.

(3) The selectivities of CO and C_2 (C_2H_2 and C_2H_4) could be adjusted by changing the ratio of CH_4 and CO_2; the H_2/CO ratio increased with an increase of CH_4/CO_2 ratio in feedstock.

(4) The energy efficiency is improved by increasing input power of microwave, but it peaked 1.56 at a fixed feed composition of ($120CH_4 + 80CO_2$) mL/min and a pulse duty factor of 100 ms/100 ms.

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