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전자파 플라즈마 토치를 이용한 이산화탄소와 메탄의 Syngas 합성

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Conversion of CO_2 and CH_4 to Syngas by Making Use of Microwave Plasma Torch

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Abstract

Carbon dioxide (CO_2) and methane (CH_4) are two major greenhouse gases. $CO_2$is a stack gas of many industrial processes and the main product of the hydrocarbon combustion. There is recent research interest on the synthesis gas (syngas) formation from CO_2 and CH_4 via the following reaction: $CH_4 + CO_2 \rightarrow 2H_2 + CO$, in order to reduce the greenhouse effects and to synthesize various chemicals, Preliminary experiments were conducted on the conversion of CO_2 and CH_4 to syngas by making use of a microwave plasma torch at atmospheric pressure. Conversion rates of $CO_2$and CH_4 to hydrogen (H_2), carbon monoxide (CO) and higher hydrocarbons were investigated using Gas Chromatography (GC) and Fourier Transform Infrared (FTIR). The experimental data indicate that the main products were H_2, CO and small amount of higher hydrocarbons, such as ethylene (C_2H_4).

Key Words : microwave plasma torch, conversion of CO_2 and CH_4,

1. Introduction

CH_4 is the major component of natural gas and one of the possible alternative energy sources. However, among all greenhouse gases, CH_4 with CO_2 also contributes most of the man-made greenhouse effect. Any utilization process of both CH_4 and CO_2 may achieve the objectives of slowing down the build-up of greenhouse gases in the atmosphere and better carbon-resource utilization. CO_2 reforming of CH_4 to synthesis gas has recently attracted considerable interest as one method of solving this objective, but this process is very energy-extensive due to the high reaction temperature [1]. Most research interests focus on the syngas formation from CH_4 and CO_2 via following reaction:

$$CH_4 + CO_2 \rightarrow 2H_2 + CO$$

Reforming of hydrocarbon fuels and synthesis of methanol, ethylene or hydrogen from CH_4 has been considered of importance because these products can be used as valuable chemicals, automobile fuel, etc [2~4]. At present, most commercial processes for the conversion of CH_4 to useful products are indirect processes in which $CH_4$is first converted to syngas, a mixture of CO and H_2 [5].

There are usually two ways for plasma CH_4 conversion, one is the indirect plasma CH_4 conversion to higher hydrocarbons, liquid fuels or other chemicals by way of synthesis gas such as dry reforming, and the other is direct plasma CH_4 conversion to more valuable liquid hydrocarbons such as oxygenates, CH_4or other liquid fuels. The various kinds of electric sources were used such as AC, DC, or pulse power supply, and also the various kinds of discharge method were used such as corona discharge, glow discharge, or dielectric-barrier discharge [1]. A new method, an atmospheric microwave plasma torch is presented in this paper for conversion of CO_2 and CH_4into syngas. The atmospheric microwave plasma torch has high efficiency. Results of computer simulations exhibit the effectiveness of the conversion models proposed in the present study. However, plasma chemistry and kinetics of CH_4 conversion in our experiment are yet to be analyzed.

2. Experimental

The design and operation of the atmospheric-pressure microwave plasma-torch are briefly summarized here for completeness, although they have been discussed in detail in previous literatures [6~10]. The main parts of experimental configuration for conversion of CO_2 and CH_4 are shown schematically in Fig. 1, which consist of a microwave plasma torch, apparatus for sample analysis, and a fume hood.

The microwave plasma-torches are generated by a 2.45 GHz magnetron, a circulator, a three-stub tuner, a tapered waveguide, and a plasma reactor. The microwave radiation from the magnetron passes through the three-stub tuner and the circulator, is guided through a tapered waveguide, and enters the discharge tube made of a fused quartz. The center axis of the quartz dielectric tube with an outer diameter of approximately 17 mm is located one-quarter wavelength from the shorted end of the waveguide and is perpendicular to the wide waveguide walls. The electric field induced by the microwave radiation in the quartz tube can be maximized by adjusting the three-stub tuner.

Also, the reflected power can be adjusted with the three-stub tuner to be less than 1% of the forward power. Even with all the tuning stubs completely withdrawn, reflected power is typically less than 10%. The igniter, a 15 kV AC electric spark system with its terminal electrodes inside the discharge tube by $N_2$and Ar gases, is fired to initiate plasma generation with the microwave radiation from the magnetron. The generated plasma inside the discharge tube is stabilized by the swirl gas input. The swirl gas enters the discharge tube sideways, creating a vortex flow in the discharge tube, stabilizing the torch flame in the center of the tube, and keeping the torch flame off the discharge tube walls. CO_2 and CH_4 gases controlled by the mass flow controller (MFC) are injected through the gases mixing vessel shown in Fig. 1, which guides CO_2 and CH_4 into the center part of the flame. The conversions in this system were defined as: [1, 11]

$$\text{Conversion of } CH_4 = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of } CH_4 \text{ introduced}} \times 100$$

$$\text{Conversion of } CO_2 = \frac{\text{moles of } CO_2 \text{ consumed}}{\text{moles of } CO_2 \text{ introduced}} \times 100$$

The selectivity is calculated based on carbon converted as: [1]

$$\text{Selectivity of } CO = \frac{\text{moles of CO formed}}{\text{moles of } CH_4 \text{ converted} + \text{moles of } CO_2 \text{ converted}} \times 100$$

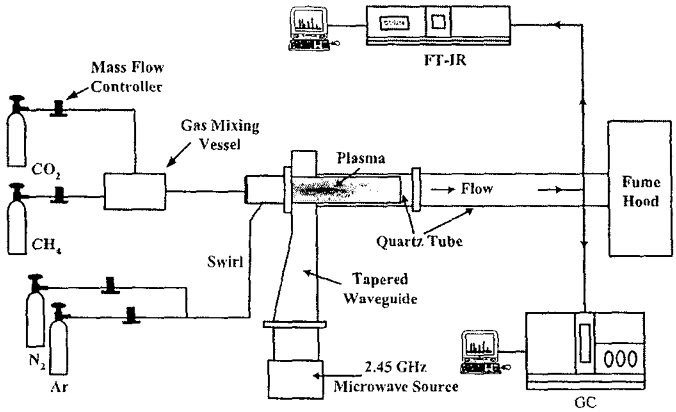

Fig. 1 Schematic diagram of microwave plasma-torch conversion system.

As shown in Fig. 1, FT-IR and GC are used in the system for an in-depth understanding of the plasma conversion process. In order to sample various by-product gases collected in a sampling bag during 10 seconds after the microwave discharge, an extractive sampling technique is employed. The extraction gas for data measurement was cooled to the room temperature. The gas extracted from the torch exit enters FT-IR and GC through stainless steel tube. The lines were long enough for the gas to be cooled to the room temperature.

3. Results and Discussions

As mentioned earlier, FT-IR and GC are employed to identify conversion of CH_4 and CO_2 concentration and changes of the plasma by-product during the time intervals of plasma discharge on and off.

Fig. 2 shows two infrared transmittance spectra, demonstrating the microwave plasma torch conversion of CH_4 and CO_2. A baseline, indicated by a gray line, was established first for the plasma off case. 7 lpm of Ar gas as a swirl gas, 60 sccm of CH_4 and 60 of sccm CO_2 as an input gas were injected. The experiment was carried out three times. Thus, each spectrum in Fig. 2 represents an average value of three data. The transmittances of the CH_4 and $CO_2$are high when there is no plasma electric discharge. After the microwave plasma was turned on and the swirl gas was injected, the gas stream was analyzed.

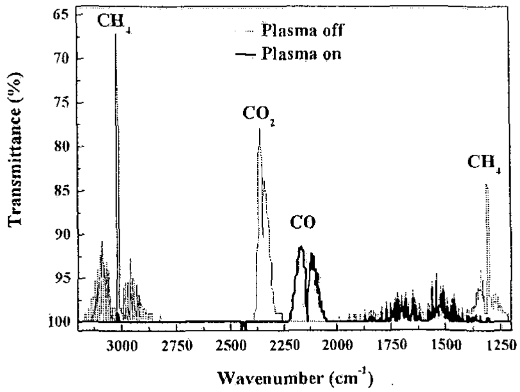

Fig. 2 FT-IR spectra showing changes of CH_4 and CO_2 concentration before and after plasma discharge for CH_4flow rate = 60 sccm; CO_2 flow rate = 60 sccm; Ar swirl flow rate = 7 lpm, microwave power = 1.0 kW.

As expected, the plasma torch flame generated by microwave radiation of 1.0 kW power destroyed most of CH_4 and CO_2molecules. The destruction rate is almost 100%. The dark line shown in Fig. 2 is the transmittance spectrum when the microwave plasma was turned on.

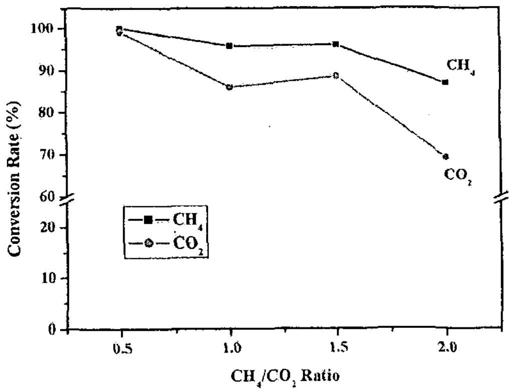

Fig. 3 Conversion rate versus CH_4/CO_2 Ratio.

Fig. 3 shows two lines of conversion rate by CH_4/CO_2 Ratio. A square dot line is CH_4 and a circle dot is CO_2. As shown Fig. 3, CH_4 and CO_2 conversion rate are very high. This experiment carried out four times. Fig. 4 shows ppm ($\times 10^4$) of H_2, CO and C_2H_4 by CH_4/CO_2 Ratio. As expected, H_2, CO and C_2H_4 syngases are created by microwave plasma discharge. The syngas made mostly of H_2 and CO occurs at the CH_4/CO_2ratio around unity with less production of C_2H_4, as expected.

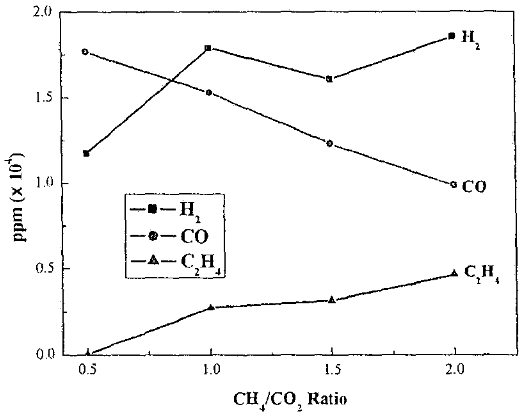

Fig. 4 ppm (× 10^4) of H_2, CO and C_2H_4 by CH_4/CO_2 Ratio.

After the microwave plasma was turned on and the swirl gas was injected, the gas stream was analyzed. As expected, the plasma torch flame generated by microwave radiation of 1.2 kW power destroyed almost all of CH_4 and CO_2contaminants. The destruction rate is close to 100%. The dark line shown in Fig. 5 is the intensity spectrum when the microwave plasma was on.

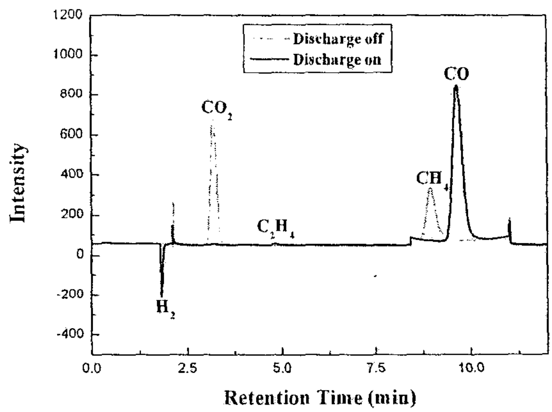

Fig. 5 GC spectra showing changes of CH_4 and CO_2 concentration before and after plasma discharge for CH_4flow rate = 60 sccm; CO_2 flow rate = 60 sccm; Ar swirl flow rate = 10 lpm; N_2 swirl flow rate = 2 lpm, microwave power = 1.2 kW.

A typical result of by-product analysis is presented in Fig. 5, which shows the gas chromatography (GC) intensity of plasma by-products from quartz tube as shown Fig. 1. Similar to Fig. 2, 10 lpm of Ar and 2 lpm of N_2 gas as a swirl gas, 60 sccm of CH_4 and 60 of sccm CO_2 as an input gas were injected into the microwave plasma torch for the data in Fig. 5. Gas sample collected in a samplingbag during 10 seconds after the microwave discharge was analyzed.

4. Conclusions

Preliminary experimental results and characteristics for plasma conversion of CH_4 and CO_2in the atmospheric-pressure microwave plasma-torch have been presented in this article. As expected, the plasma torch flame generated by microwaves of 1.2 kW power disintegrates most of the CH_4 and CO_2 molecules, indicating the destruction efficiency close to 100% and converting the contaminants to CO and H_2. A conversion experiment at large flow rate will be carried out in future for practical applications.

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