Korean J. Chem. Eng., **21**(3), 670-675 (2004)

Steam Plasma Reforming of Biogas by Non-Thermal Pulsed Discharge

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(*Received 17 December 2003 • accepted 23 February 2004*)

Abstract−The purpose of this study was to develop technology that can convert biogas to synthesis gas (SynGas), a low emission substituted energy, using a non-thermal pulsed plasma method. To investigate the characteristics of the SynGas production from simulated biogas, the reforming characteristics were studied about the variations of pulse frequency, biogas component ratio (C_3H_8/CO_2), vapor flow ratio (H_2O/TFR), biogas velocity and pulse power. A maximum conversion rate of 49.1% was achieved for the biogas when the above parameters were 500 Hz, 1.5, 0.52, 0.32 m/s and 657 W, respectively. Under the above-mentioned reference conditions, the dry basis concentrations of the SynGas were, H_2 64.5%, CH_4 8.1%, C_2H_2 6.7%, C_3H_6 4.9%, CO 0.8% and C_2H_4 0.4%. The ratio of hydrogen to the other intermediates in the SynGas (H_2/ITMs) was 3.1.

Key words: Biogas, Non-thermal Plasma, Plasma Reforming, SynGas, Pulse Corona

INTRODUCTION

With the development of industrial and scientific techniques, the demands for energy have gradually increased. Therefore, there is the need to develop, without delay, alternative energy sources to fossil fuels, due to their restricted abundance. Studies on alternative energy development, such as solar and wind energy, have progressed since the beginning of the 1980s. With the greater understanding, in recent years, of new environmental treatments, the technology for the use of biogas, which is produced from landfill and anaerobic reactors for the treatment of wastewaters and foods, has raised interest in its use as an alternative energy source.

At present, most gases produced from the wastewater treatment field and landfill are burned as flares, while part is used as a source for heating and generation within boiler systems. However, where biogas is directly burned as a heat source, much air pollution is generated due to its low combustibility and impurities content, such as ammonia etc. Also, there is a problem with uniform energy supply, due to boiler fluctuations that are generated when the biogas composition is not uniform. Therefore, such biogas is more usefully converted to SynGas, which improves the quality over direct burning. Consequently, there is a demand for the development of advanced reforming technology, which could possibly produce alternative energy and reduce the odor quantity and greenhouse gases emissions by the safe treatment of biogas.

There are several kinds of reforming methods for SynGas, such as partial oxidation [Czernichowski, 1999], CO_2 reforming [Fridman and Rusanov, 1994], steam reforming [Cormier and Rusu, 2003] and non-thermal plasma (NTP) reforming [Czernichowski and Czernichowski, 1999; Bae-Bok Hwang et al., 2003]. Although steam reforming is currently much used, due to having the merits of the gas treatment quantity and hydrogen production rate, this method also has the disadvantages of the requirements of high temperature and pressure, and a catalyst, to increase of the hydrogen conversion. However, contrary to steam reforming, NTP reforming has characteristics where a catalyst is not used, and temperature and pressure in reactor are below 1,200 °C and 6 bar, respectively.

In this study, advanced steam NTP reforming technology was developed for the conversion of biogas to SynGas, which is an alternative energy source, with a high quality and low emissions. Also, to present good operating conditions, parametric screening studies were conducted on the variations of pulse frequency, biogas component ratio, vapor flow ratio, gas velocity and pulse power, which all affect the biogas conversion.

THEORY AND EXPERIMENTAL METHOD

1. Reforming Reactions

The simulated biogas used in this study consists of C_3H_8 (propane), C_3H_6 (propylene) and CO_2 (carbon dioxide). Through the reactions listed below, H_2 (hydrogen), CH_4 (methane), C_2H_2 (acetylene), CO (carbon monoxide) and C_2H_4 (ethylene) are produced.

① Steam reforming reaction

$$C_3H_8+3H_2O \rightarrow 3CO+7H_2 \tag{1}$$

[Czernichowski and Czernichowski, 1999]

$$C_3H_6+3H_2O \rightarrow 3CO+6H_2 \tag{2}$$

② CO_2 reforming reaction

$$C_3H_8+3CO_2 \rightarrow 6CO+4H_2 \tag{3}$$

[Czernichowski and Czernichowski, 1999]

$$C_3H_6+3CO_2 \rightarrow 6CO+3H_2 \tag{4}$$

③ Pulse plasma reforming (cracking) reaction

$$C_3H_8 \rightarrow C_3H_6+H_2 \tag{5}$$

[Czernichowski and Czernichowski, 1999]

$$C_3H_8 \rightarrow CH_4+C_2H_2+H_2 \tag{6}$$

$$C_3H_8 \rightarrow CH_4+C_2H_4 \tag{7}$$

[Barsan and Thyrion, 2003]

$$C_3H_6 \rightarrow CH_4+C_2H_2 \tag{8}$$

④ Single and inverse vapor shifting reaction

$$CO+H_2O \rightarrow CO_2+H_2 \tag{9}$$

[Czernichowski and Czernichowski, 1999]

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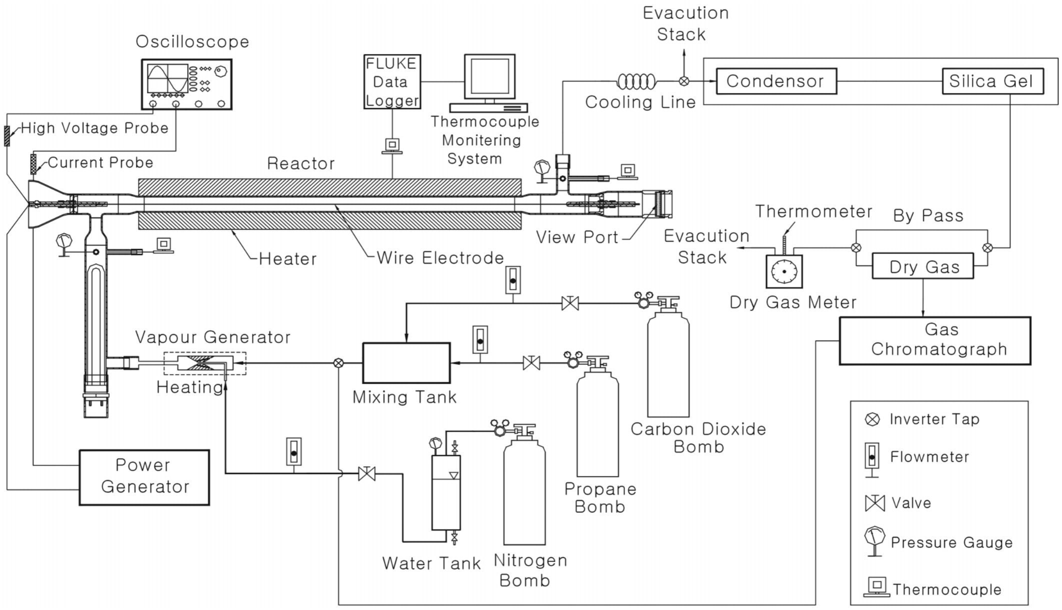


Fig. 1. Schematic of the experimental setup.

2. Biogas Conversion Rate

The biogas conversion rate can be calculated by Eq. (10).

$$\eta(\%) = \left[\frac{V_{in} - V_{out}}{V_{in}}\right] \times 100 \quad (10)$$

where, V_{in} is the C_3H_8 or CO_2 volume input (Nm^3) and V_{out} is the C_3H_8 or CO_2 volume output (Nm^3).

3. Calculation of Pulse Power

The pulse power is calculated as follows, Eq. (11).

$$P(W) = \frac{1}{2}Cv^2f \quad (11)$$

where, v is the pulse voltage (V), f is the pulse frequency (Hz) and C is the capacitor (1EA=3,6000×10^{-12} F). In this study, the pulse power was three times that of the value of Eq. (11) because the same three capacitors were used.

4. Experimental Setup

Fig. 1 shows an experimental apparatus set-up that can be used to construct an experiment for steam pulse plasma reforming. This consists of a wire type reforming reactor, pulse power supply equipment, simulated gas/steam feeding line and measurement/analysis line.

A wire type reforming reactor has been made of stainless pipe, with a length and diameter of 1 m and 43.8 mm, respectively. The discharge electrode of ϕ0.5 mm, made from Ni-Cr wire, was inserted at the center of the reactor, and an electric heater outside of the reactor.

The pulse power supply equipment consisted of a power regulator, high voltage DC generator, pulse generator and pulse transformer. The maximum voltage, pulse length and maximum frequency were 50 kV, 600 ns, 900 Hz, respectively.

The simulated gas/steam feeding line consisted of a mixing tank and steam generator. The mixing tank was used to mix propane and carbon dioxide, and the steam generator produced the vapor and mixed the simulated gas.

The measurement/analysis line consisted of electric characteristics and temperature measurements and gas analysis. The electric characteristics were measured by a voltage probe (Tektronix P6015A), a current probe (Tektronix A6303) and a digital oscilloscope (Tektronix TDS 3052). The temperature measurements were taken with a 0.3 mm K-type thermocouple, with a data logger (Fluke Hydra Data Logger). The gas analyses were accomplished by using gas chromatography and a sampling line.

5. Experimental Method

The main experiment was performed after the reforming reactor had been stabilized at 800 °C by electrical heating for 2 hours. The initial operating characteristics are shown in Fig. 2.

The electric characteristics of the pulse voltage and frequency were controlled by the knob on the pulse power supply equipment.

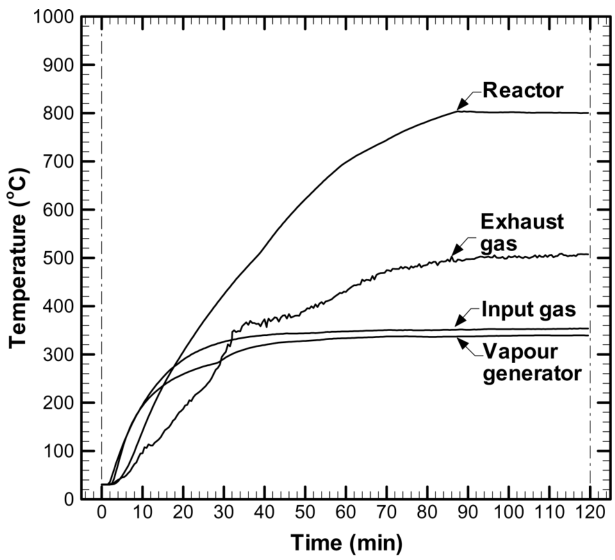


Fig. 2. Initial operating characteristic of the reformer.

Table 1. Experimental conditions and data for the reference condition

Experimental condition					
Conditions	Pulse frequency (Hz)	Component ratio (C_3H_8/CO_2)	Vapor flow ratio (H_2O/TFR^a)	Biogas velocity (m/sec)	Pulse power (W)
Value	500	1.5	0.52	0.32	657

Experimental data								
SynGas concentration (%)						Biogas conversion rate[b] (%)		H_2/ITMs[c]
H_2	CH_4	C_2H_2	C_3H_6	CO	C_2H_4	$\eta_{C_2H_6}$	η_{CO_2}	
64.5	8.1	6.7	4.9	0.8	0.4	49.1	42.3	3.1

[a]TFR : Total flow rate (*l*/min), i.e., Biogas+H_2O
[b]Calculated by Eq. (10)
[c]ITMs : Intermediates, i.e., $CH_4+C_2H_2+C_3H_6+CO+C_2H_4$

The voltage, current and frequency were measured by a high voltage probe and a current probe and an oscilloscope, respectively. Propane and carbon dioxide, which are the components of the simulated biogas, were fed from their respective bombs, through a flow meter, and mixed in the mixing tank. Water was fed into the steam generator, which was converted to form the vapor flow. The water flow rate was controlled by a metering valve. The simulated biogas and vapor produced were mixed in the steam generator. The mixed gas, including the vapor, was fed to the reforming reactor. Sampling of the SynGas was achieved at a sampling port installed at the reactor exit. The sampling gas passed through a cooler to remove any water, and was then analyzed by gas chromatography (Shmadzu 14B). The analyses of the H_2, CO, C_3H_8, CO_2, CH_4, C_2H_2, C_2H_4 and C_3H_6 were accomplished, with a Molecular Sieve (5A 80/100 mesh) and HayeSep R (100/120 mesh) columns, with thermal conductivity detection. The reactor, inlet and outlet of the reactor and the steam generator temperature measurements were taken by using 0.3 mm Pt/Pt-13% Rh thermocouples, with a data logger (Fluke 2625A).

Experimental reference conditions were found through pretests. These conditions were as follows (refer to Table 1): Reactor temperature 800 °C; propane, carbon dioxide and vapor are feeds of 9, 6 and 13.7 *l*/min, respectively. The frequency, voltage and pulse power were 500 Hz, 15.6 kV and 657 W, respectively. The pulse power was calculated by using Eq. (11). Parametric screening studies were also performed to find the optimum pulse frequency, biogas component ratio (C_3H_8/CO_2), vapor flow ratio (H_2O/TFR), biogas velocity and pulse power that affected the reforming characteristics of the biogas, which ranged between 330-600 Hz, 0.67-2.3, 0.42-0.52, 0.28-0.35 m/sec and 270-657 W, respectively.

RESULT AND DISCUSSIONS

Our reference conditions, having the best biogas conversion rate, were selected from the results of repeated experiments with various biogas reforming characteristics, using steam plasma reforming. The experimental conditions and results are shown in Table 1.

The SynGas concentration produced from the biogas reforming under the reference conditions were: H_2 64.5%, CH_4 8.1%, C_2H_2 6.7%, CO 0.8%, C_3H_6 4.9% and C_2H_4 0.4%. The majority of the SynGas is known to be hydrogen, and the hydrogen to intermediates ratio (H_2/ITMs) was 3.1. Also, the conversion rates of propane and carbon dioxide, which are the components of biogas, were 49.1 and 42.3%, respectively.

Parametric screening studies were performed with variations of the pulse frequency, biogas component ratio, vapor flow ratio, biogas velocity and pulse power, which could potentially influence the reforming characteristics of the biogas. The results were as follows.

1. Pulse Frequency

Fig. 3 presents the results of the variations in the pulse frequency only. The frequency was varied from 300 to 600 Hz, with the other parameters fixed at there reference conditions.

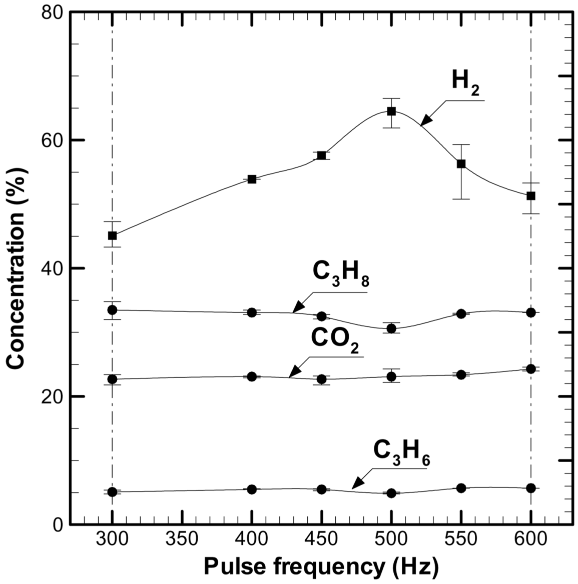
Fig. 3(a) shows the concentration of the selected gases in the produced SynGas. As already mentioned, the simulated gas consisted of C_3H_8, C_3H_6 and CO_2, with a component composition of 57, 2.7 and 40%, respectively. Although the concentration of the biogas changed slightly, the C_3H_8 and CO_2 were reduced as 30.6-33.5 and 22.7-24.3%, respectively, when the pulse frequency was impressed. However, a little C_3H_6 increases as 4.9-5.7% by cracking reaction which is plasma reforming reaction of Eq. (5), compared with the decrease by reforming reaction of vapor and carbon dioxide [refer to Eq. (2) and Eq. (4)].

At a pulse frequency of 500 Hz, the average H_2 concentration showed a maximum value of 64.5%, while the average C_3H_8 and C_3H_6 concentrations showed minimum values of 30.6 and 4.9%, respectively, but the CO_2 concentration remained almost unchanged at 23.1%. This was because C_3H_8 and C_3H_6 are converted to H_2, not by carbon dioxide reforming, but by vapor and cracking reforming.

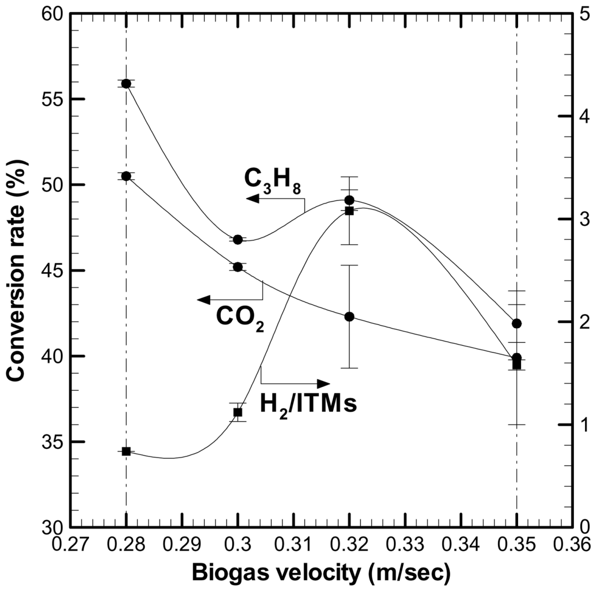
Fig. 3(b) presents the biogas conversion rates and H_2/ITMs ratios. At a pulse frequency of 500 Hz, the conversion rate of C_3H_8 had a maximum value of 49.1%, but the maximum CO_2 conversion rate was 43.3%, at a pulse frequency of 450 Hz. Therefore, at a pulse frequency of 500 Hz, most of the H_2 conversion was achieved by a greater proportion of vapor and cracking, than carbon dioxide reforming. Also, at a pulse frequency of 500 Hz, the maximum H_2/ITMs ratio was 3.1, suggesting the hydrogen was converted more than the intermediates.

2. Biogas Component Ratio

Fig. 4 presents the results for the various biogas component ratios (0.67-2.3) for the simulation of various kinds of biogas, with all the other parameters maintained at the reference conditions.

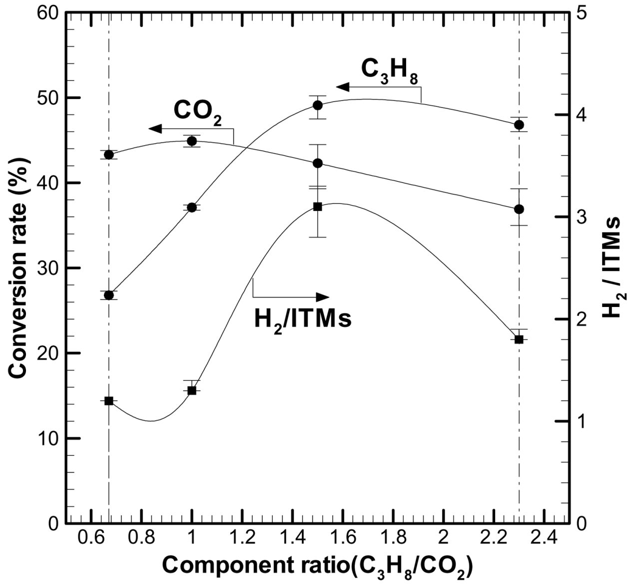


(a) Concentration of selected SynGas

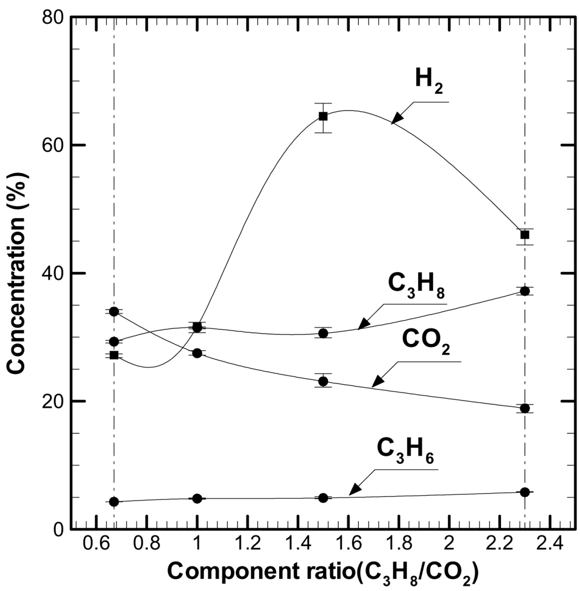


(b) Biogas conversion rate and H_2/Intermediates ratio

Fig. 3. Effect of the various pulse frequencies.



(a) Biogas conversion rate and H_2/Intermediates ratio



(b) Concentration of selected SynGas

Fig. 4. Effect of the various component ratios.

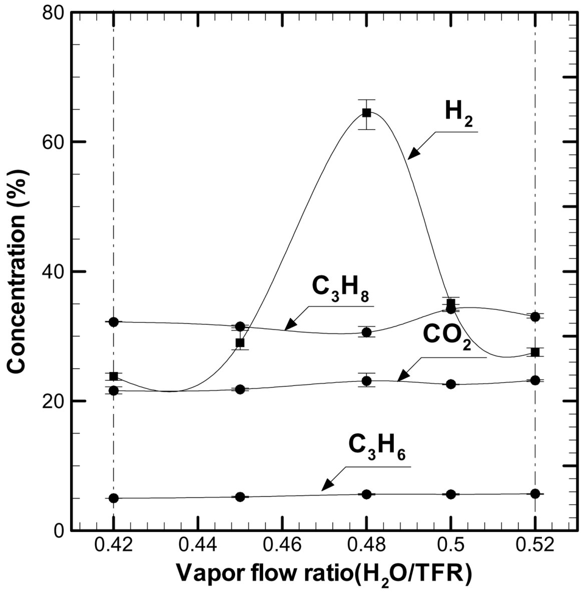
Fig. 4(a) shows the biogas conversion rates and H_2/ITMs ratios. Both the C_3H_8 and CO_2 conversion rates increased with increasing biogas component ratios. The C_3H_8 and CO_2 conversion rates had maximum values when the biogas component ratios were 1.5 and 1, respectively. The C_3H_8 conversion rate was also larger than that for CO_2, according to increases in the component ratio. This was the reason for the increase in the C_3H_8 with increasing component ratios. The H_2/ITMs ratio also showed a similar pattern to the C_3H_8 conversion rate, with a maximum component ratio value of 1.5, which could be confirmed by the H_2 concentration in Fig. 4(b).

Also, as expected, the C_3H_8 concentration increased, and the CO_2 concentration decreased gradually, due to the increase in the feeding propane with higher biogas component ratios. Therefore, it has been found that the operation conditions should be changed for the effective reforming of various biogas compositions.

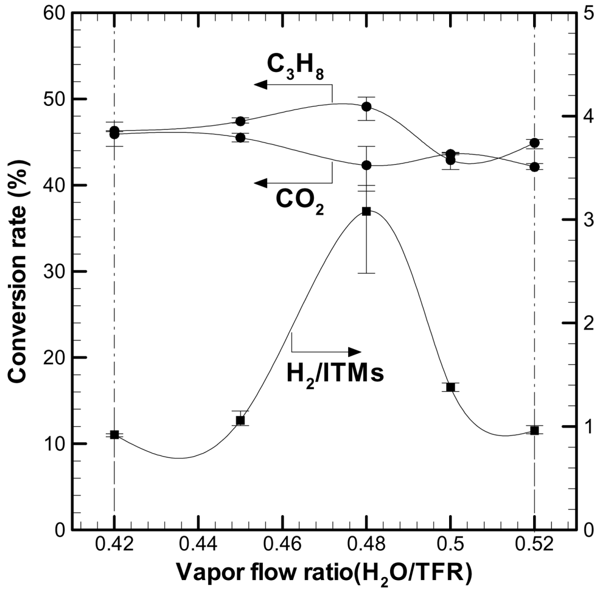
3. Vapor Flow Ratio

Fig. 5 shows the results where the vapor flow ratio was changed from 0.42 to 0.52, in order to find the reforming characteristics for various vapor quantities.

As can be seen in Fig. 5(a), the H_2 concentration was drastically increased with increases in the vapor flow ratio. The H_2 concentration was found to have a maximum value with a vapor flow ratio of 0.48. The reason for this was that the vapor reforming [refer to Eqs. (1) and (2)] and single vapor shifting reactions of Eq. (9) are

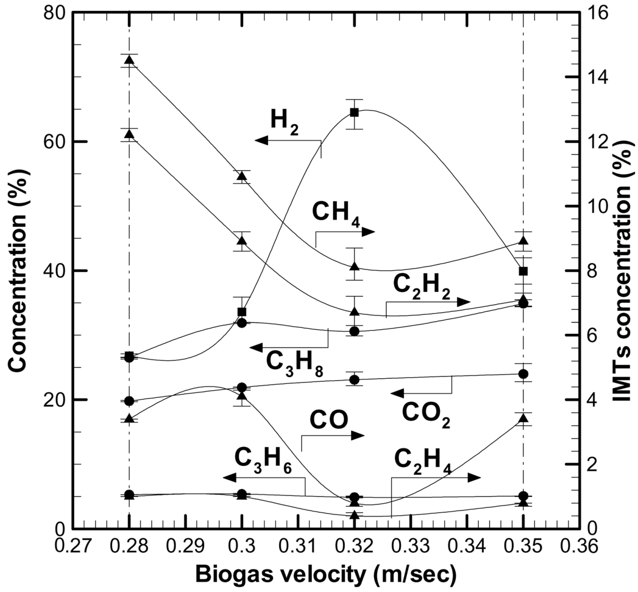


(a) Concentration of selected SynGas

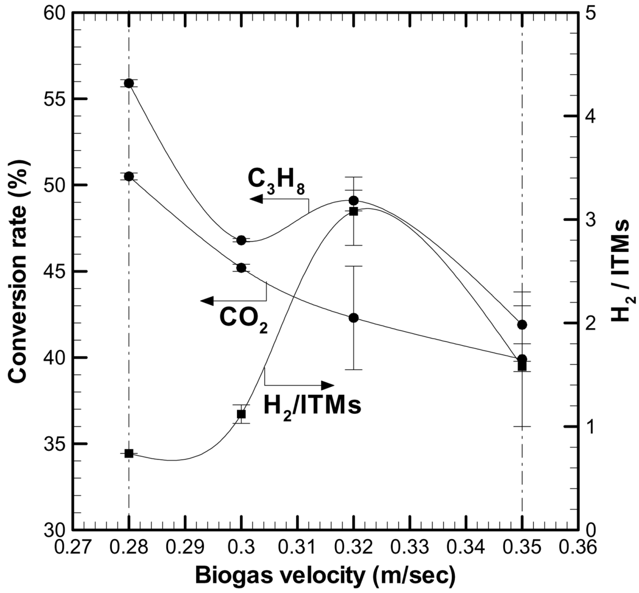


(b) Biogas conversion rate and H_2/Intermediates ratio

Fig. 5. Effect of the various vapor flow ratios.



(a) Concentration of selected SynGas



(b) Biogas conversion rate and H_2/Intermediates ratio

Fig. 6. Effect of the various biogas velocities.

the first of the reactions. However, the H_2 concentration was drastically decreased with increasing vapor flow ratios. This was because the reforming reaction was not effective due to low concentration densities of C_3H_8 and C_3H_6, which were the major components for the production of H_2 when the vapor quantity increased. The concentration of C_3H_8 showed a minimum value at the vapor flow ratio where the H_2 concentration was at a maximum value, which was due to the major reaction being the conversion of C_3H_8 to H_2. This could be worked out from the C_3H_8 conversion rate in Fig. 5(b). However, the CO_2 concentration and conversion rate remained almost unchanged with variations in the vapor flow rate.

4. Biogas Velocity

Fig. 6 shows the experimental result when the biogas velocity flow into the reactor was changed from 0.28 to 0.35 m/sec. An increase in the biogas velocity results in a decrease in the HRT (hydraulic residence time) because the diameter of the reactor does not change.

As can be seen in Fig. 6(a), the H_2 concentration increased with increases in the biogas velocity gradually, and a maximum value of that encountered. The reason for this was that the biogas quantity was increased with increasing the biogas velocity. This was also confirmed by the result for the H_2/ITMs ratios in Fig. 6(b). The H_2 concentration also decreased when the biogas velocity was increased, as it is difficult to have a good reforming reaction, due to the reduced HRT of the reactor.

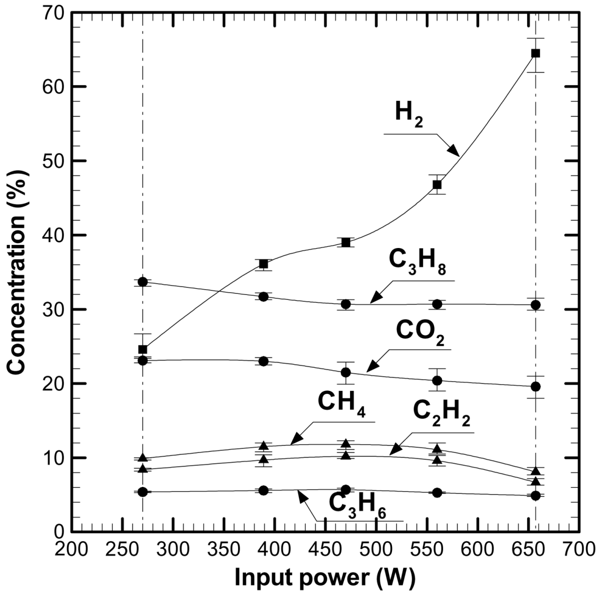
Although the peak point for the H_2 concentration was at a biogas velocity of 0.32 m/s, as seen in Fig. 6(b), its maximum value was at a biogas velocity of 0.28 m/s. The reason for this was that there was enough production time for the intermediates with a larger HRT, as can be found from the concentrations of CH_4, C_2H_2 and C_2H_4 in Fig. 6(a). However, the CO_2 conversion rate for the biogas was continuously decreased with increasing biogas velocity.

5. Pulse Power

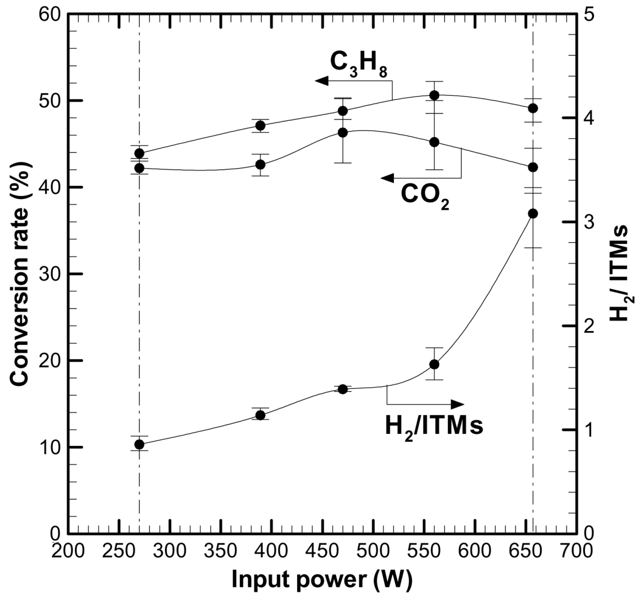
Fig. 7 shows the results when the pulse power was changed from 270 to 657 W. The pulse power was calculated by using Eq. (11), as mentioned earlier.

The H_2 production increased, while the concentration of C_3H_8 gradually decreased, when the pulse power was increased, as shown in Fig. 7(a). The reason for this was that the reforming reaction rapidly progresses with increases in the radicals, which have strong reactivity due to the increased electrical energy in the reactor.

The H_2/ITMs ratios increased with increases in the pulse power, as seen in Fig. 7(b). This means that the hydrogen in clean fuel increases, while the intermediates relatively decrease. Even though it is difficult to know the exact results from Fig. 7(b), the conversion rate for the biogas had a maximum value at all voltage points, as shown by the intermediate concentrations of the CH_4 and C_2H_2.



(a) Concentration of selected SynGas



(b) Biogas conversion rate and H_2/Intermediates ratio

Fig. 7. Effect of the various input powers.

CONCLUSIONS

Steam plasma biogas reforming was studied by using an NTP pulse discharge, and the results were as follows:

The composition of the SynGas produced was: H_2 64.5%, CH_4 8.1%, C_2H_2 6.7%, C_3H_6 4.9%, CO 0.8% and C_2H_4 0.4%, at the optimum conditions for biogas conversion. The conversion rates for propane and carbon dioxide were 49.1 and 42.3%, respectively, and the H_2/ITM ratio was 3.1.

The reforming characteristics at various pulse frequencies, biogas component ratios, vapor flow ratios, biogas velocities and pulse powers were studied. The biogas conversion rate increased, and had a maximum value, when all of the parameters, with the exception of the pulse power, were increased. The optimum values were 500 Hz, 1.5, 0.52 and 0.32 m/s, respectively. In the case of the pulse power, the biogas conversion rate was increased gradually as it increased. The H_2/ITMs ratio had its highest value at the maximum conversion rate for the biogas for all the parameters.

ACKNOWLEDGMENTS

This study was supported by research funds from Chosun University, 2003.

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