Reforming Characteristics for Hydrogen Production Using Plasmatron

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Abstract: A high-temperature plasma torch (a so-called plasmatron) was designed for a hydrogen production reformer. Experiments were carried out to determine the optimal operating conditions producing the maximum amount of hydrogen. The maximum values of the H_2, CO, H_2 yield and the energy conversion efficiency were 30.9, 20.2, 97.7, and 40.5 %, respectively. Parametric studies were performed regarding the effects of vapor, carbon dioxide, and catalyst addition in the reactor, respectively. In the case of vapor reforming, H_2 was mostly unchanged with an average value of 29.2 %. However, CO was reduced as $6.6 \sim 8.6$ %, while CO_2 was increased with the increase of the vapor flow rate. For carbon dioxide reforming, H_2 was decreased with the increase of the CO_2 flow rate, but CO and CO_2 gradually increased. For reforming with the nickel catalyst, the amount of H_2 produced was slightly larger than without catalyst addition in the reactor, while the CO and CO_2 contents were lower, due to the increase of residence time and adsorption.

Keywords: reforming, hydrogen, plasma torch, fuel cell

Introduction

Because the sources of energy are limited worldwide, the development of alternative energy is a very important issue in regard to the depletion of fossil fuel resulting from the rapid increase in energy consumption. Among the numerous research studies on the development of alternative energy, the conversion to synthesis gas by reforming hydrocarbon fuels and techniques producing high concentrations of hydrogen are quite promising. Recognized as a clean fuel, hydrogen is anticipated to be the major next-generation energy source [1]. In addition, because it can be used in most energy systems, it may be considered to have the most appropriate characteristics for use as a substitute for conventional fossil fuel energy systems.

Research into the production of hydrogen by reforming fuels has been carried out using various methods, such as steam reforming [2], partial oxidation reforming [3], and carbon dioxide reforming [4]. Recently, with the increased interest in plasma techniques, plasma torch [5],

gliding arc plasma [6], and DBD (Dielectric Barrier Discharge) [7] technologies have been applied to reforming with the techniques listed above.

Among reforming methods, currently steam reforming is used most frequently because of its advantages of gas treatment amount and hydrogen yield rate. Nevertheless, its reaction equipment is large, the reaction rate is relatively slow, and a high temperature and pressure are required because of the highly endothermic reaction.

A plasmatron is a reformer that converts various fuels to synthesis gas containing abundant hydrogen by applying partial oxidation reforming [8]. The heat of the plasma itself and the internal reaction heat due to partial oxidation are used during the reforming in a plasmatron. Because of its fast starting and response times within a few seconds, it is applicable to a wide range of flow rates, and is particularly useful for the small scale systems, such as the reformer in a residual fuel cell, which needs fast response characteristics [9].

In this study, a high-temperature plasmatron was designed for a hydrogen production reformer. Hydrogen gas was produced by reforming propane using the plasmatron, and the optimal operation conditions for maximal hydrogen production and maximal conversion effi-

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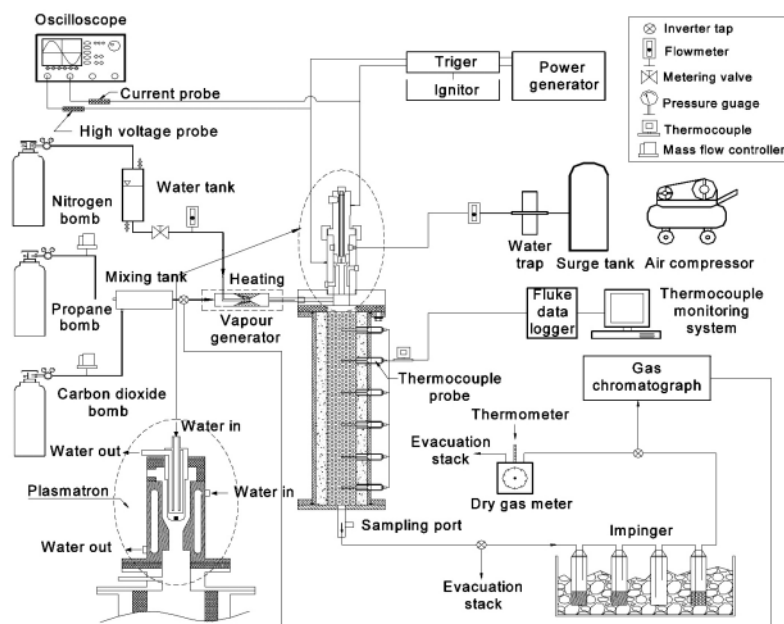 (e-mail: ynchun@chosun.ac.kr)

Figure 1. Schematic illustration of the experimental apparatus.

ciency of propane were assessed through parametric screening studies.

Experimental

Experimental Apparatus

The experimental apparatus consisted of a plasmatron reformer, electronic supply equipment, a gas and steam feeding line, and a measurement system, as shown in Figure 1.

A plasmatron reformer consists of both a plasma torch (see detailed Figure 1) and a reactor. To lessen the erosion phenomenon of electrodes caused by the high temperature, cold water was supplied to the two electrodes in the plasmatron reformer. The reactor contained six thermocouple probes and was insulated by asbestos to protect heat release. In the case of the test for catalytic reforming, the reactor was filled with 20 wt% Ni/γ-Al$_2$O$_3$ catalyst. The nickel catalyst was prepared by impregnating a solution of nickel(Ⅱ) nitrate hexahydrate (Ni(NO$_3$)$_2$ · 6H$_2$O) on γ-Al$_2$O$_3$, followed by drying at 150 ^{o}C for 30 min and calcinating in an electric furnace at 600 ^{o}C for 1 h. The nickel loading was 20 wt% for Ni/ γ-Al$_2$O$_3$.

The electronic supply equipment consisted of a power generator, an igniter, and a trigger system. The power generator could supply an electric power of 10 kW with a maximum current of 50 A and a maximum voltage 200 V. The igniter supplied a high voltage (up to 30 kV) to start the initial operation. The trigger system was used to maintain the plasma continuously.

The gas and steam feeding line allowed gas, air, and steam feeding. The gas and air feeding lines contained a metering flow controller (MFC; F201AC-FA-22-V) and a flow meter, respectively, to control the flow rates. In the case of air feeding, a surge tank was used to control the fluctuation of air fed from the compressor. The steam feeding line consisted of a nitrogen bomb, water tank, metering valve, and vapor generator. Liquid water in the water tank was compressed by high-pressure nitrogen gas, the water flow was measured by a metering valve, and the liquid water vaporized in the vapor generator.

The measurement system was divided into the measurement of electric characteristics and temperature, and the gas sampling line. The electric characteristics were measured by a high-voltage probe, a current probe, and a digital oscilloscope. The temperature was measured using an R-type thermocouple (Pt/Rh 13 %, 0.3 mm in diameter) and data analysis equipment. The gas sampling line consisted of an impinger, a dry gas meter (Shinagawa, DC-2c), and a gas chromatograph (Shimadzu, GC-14B).
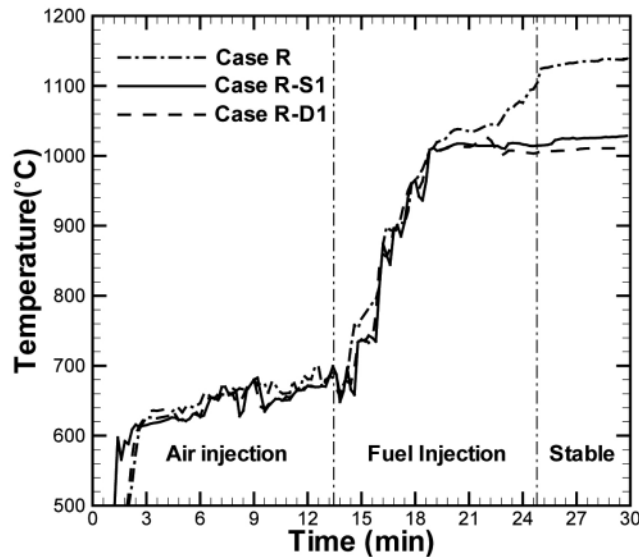
Experiment Methods

The flow rate of water compressed by high pressure nitrogen was controlled by a flow meter and fed to a vapor generator to make steam. This generated steam entered the plasmatron with a mixture of propane and carbon dioxide. Air was also fed into the plasmatron through a surge tank.

An input power of 8 kW (200 V, 40 A) was supplied by a power generator; the voltage and current were measured by a high-voltage probe and a current probe with an

Table 1. Experimental Conditions and Range

Conditions	Reference (O_2/C_3H_8 mole ratio)	Vapor effect (H_2O/C_3H_8 mole ratio)		Carbon dioxide effect (CO_2/C_3H_8 mole ratio)		Input power (kW)
	Without Cat.[a]	Without Cat.	With Cat.	Without Cat.	With Cat.	
	Case R	Case V1	Case V2	Case C1	Case C2	
Range	0.94～1.48	4.3～10		0.8～3.05		
	O_2/C_3H_8 standard	1.13				8

[a] Cat.: Catalyst

Figure 2. Initial operating characteristics of the reformer.

oscilloscope.

The temperature at the wall of the reactor was measured using thermocouple probes and data analysis equipment.

The synthesis gas was collected at the sampling port installed at the outlet of the reactor; the water content of the collected sample was measured by different weight at the impinger, and it entered the GC sampling route as dry bases and analyzed. The analysis was performed using TCD, with Molecular Sieve 5 A (H_2), Molecular Sieve 13 X (CO), and HayeSep R (CH_4, CO_2, C_2H_2, C_2H_4, C_3H_6, C_3H_8) used as analysis columns.
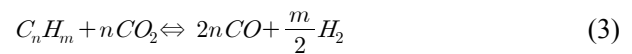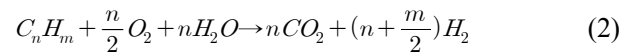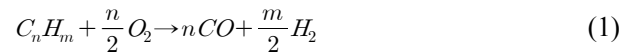
Experiments were performed for the reference, vapor effect, and carbon dioxide effect, as can be seen in Table 1. First, tests were made according to variation of the O_2/C_3H_8 mole ratio to determine the optimal reference conditions that produced the highest hydrogen concentration. Secondly, under the reference conditions, steam was added to change the H_2O/C_3H_8 mole ratio with and without the catalyst in the reactor. Thirdly, under the reference conditions, CO_2 was added to change the CO_2/C_3H_8 mole ratio, with and without the catalyst in the reactor.

Experiments were performed under constant temperature condition for each case, as can be shown in Figure

2. The temperature was stabilized at ca. 700 ^{o}C by plasma generated through the injection of air; subsequently, by injecting propane simultaneously, the reaction temperature was raised to over 1,000 or 1,200 ^{o}C and maintained continuously.

Reforming Reaction and Data Analysis

The general reforming reactions of a hydrocarbon (C_nH_m) are represented by reactions (1)～(4) [9-12]. These reactions are the partial oxidation reforming reaction, steam reforming reaction, CO_2 reforming reaction, and CO shifting reaction, respectively.

$$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2 \tag{1}$$

$$C_nH_m + \frac{n}{2}O_2 + nH_2O \rightarrow nCO_2 + (n + \frac{m}{2})H_2 \tag{2}$$

$$C_nH_m + nCO_2 \Leftrightarrow 2nCO + \frac{m}{2}H_2 \tag{3}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{4}$$

To assess the reforming effectiveness during high-temperature plasma reforming, the hydrogen yield, the energy conversion efficiency, and the conversion efficiency were calculated using Equations (5), (6), and (7), respectively [13].

$$H_2 \text{ yield } (\%) = \frac{H \text{ of reformed gas}}{H \text{ of fuel}} \times 100 \tag{5}$$

$$Energy \text{ conversion efficiency } (\%) =$$
$$\frac{Energy \text{ of reformed gas}}{Energy \text{ of fuel}} \times 100 \tag{6}$$

$$Conversion \text{ rate } (\%) =$$
$$\frac{Input \text{ concentration - Output concentration}}{Input \text{ concentration}} \times 100 \tag{7}$$
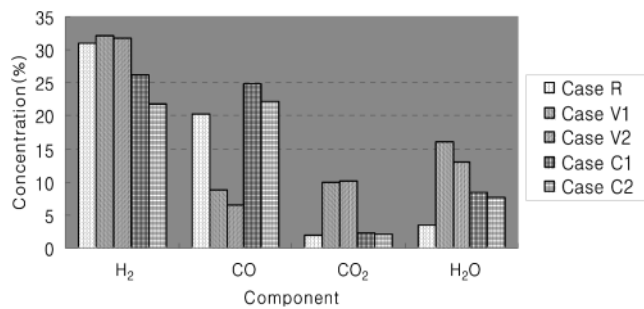
Figure 3. Concentrations of selected components in reformed gas.

Results and Discussion

A comparison between the produced gases in each case is (see Table 1) presented in Figure 3.

Cases V1 and V2, which are vapor partial oxidations like reaction (2), had the highest hydrogen (31.7~32 %) and carbon dioxide (9.9~10.2 %) productions, but the lowest concentration of CO (6.4~8.9 %). Particularly, Case V2, incorporated the nickel catalyst in the reactor, gave a lower CO concentration, when compared with the system without catalyst (Case V1). This result explains why the CO conversion reaction shown by reaction (4) prevailed when using the nickel catalyst. This situation means that Case V2 is the best reformer for a commercial fuel cell stack, such as the PEMFC. The O_2/C_3H_8 and H_2O/C_3H_8 mole ratios under optimal operating conditions were 1.12 and 7.15, respectively.
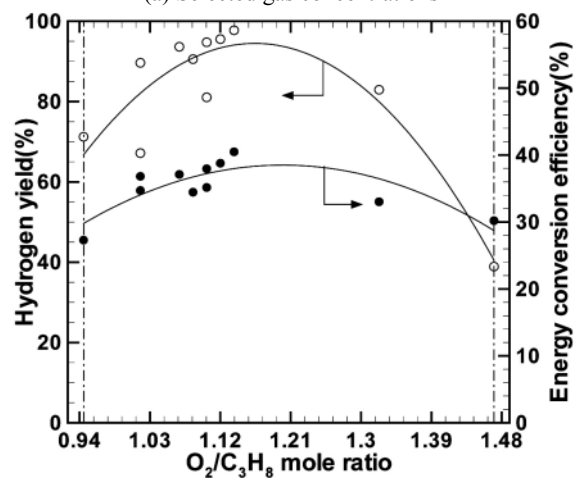
Partial Oxidation Reforming

The results of partial oxidation reforming are shown in Figure 4. The C_3H_8 content was changed from 0.9 to 1.4 L/min while the O_2 flow rate was fixed at 1.32 L/min. Therefore, the O_2/C_3H_8 mole ratio changed from 0.94 to 1.48, as in the "Reference" (Case R) in Table 1.

Figure 4(a) presents the concentrations of selected major gases in the synthesis gas according to the variation of the O_2/C_3H_8 mole ratio. The maximum value of H_2 produced was 30.9 % at an O_2/C_3H_8 ratio of 1.13. The average value of CO produced was 18.9 %. As shown in the results, the major components of the synthesis gas were H_2 and CO. The H_2/CO ratio shows a maximum value of 1.55. It was close to the complete oxidation reaction with the increase of the O_2/C_3H_8 mole ratio; hence, the concentration of CO_2 increased and the concentration of H_2 decreased.

Figure 4(b) shows the H_2 yield and the energy conversion efficiency. The maximum values of the H_2 yield and the energy conversion efficiency were 97.7 and 40.5 %, respectively, at an O_2/C_3H_8 ratio of 1.13, which is a same point for the maximum values of H_2 and CO. Therefore, the energy conversion efficiency improved
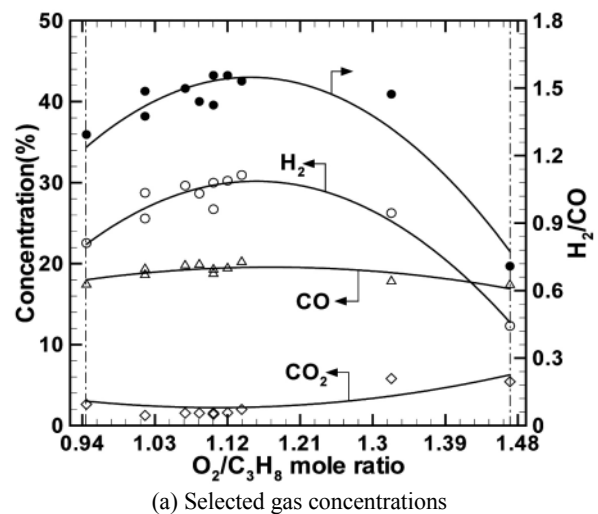
(a) Selected gas concentrations

(b) H_2 yield and energy conversion efficiency
**Figure 4.** Partial oxidation reforming.

than energy conversion rate 83.3 % in the partial oxidation of natural gas.

Experiments for the effects of vapor (H_2O/C_3H_8) and carbon dioxide (CO_2/C_3H_8) were conducted under conditions where the O_2/C_3H_8 mole ratio was 1.13, which produced highest amount of H_2.

Effect of Vapor

Figure 5 shows the results of the vapor reforming (Case V1) when steam was added to the standard conditions of Case R, without the catalyst in the reactor.

In Figure 5(a), the concentration of H_2 did not change significantly as the average value was 29.2 % upon variation of the H_2O/C_3H_8 mole ratio, which is almost the same value as that of the standard of Case R. On the other hand, the CO content was reduced as 6.6~8.6 % by ca. 50 % in comparison with Case R. The CO_2 content increased in comparison with Case R, and it increased upon increasing the H_2O/C_3H_8 ratio. In the case where steam was added to the partial oxidation reforming re-
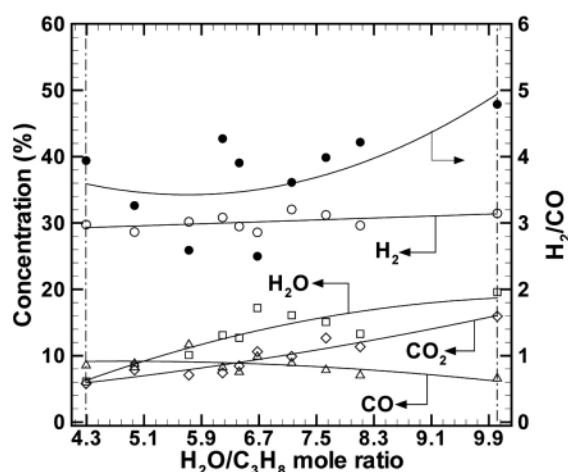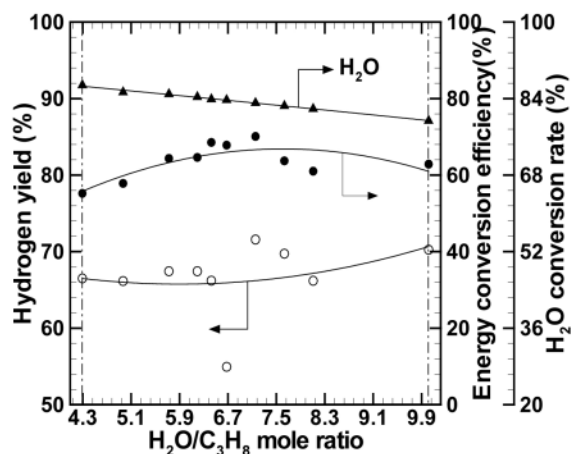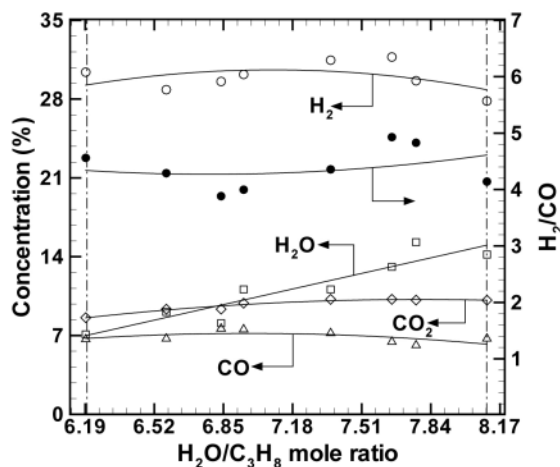
(a) Selected gas concentrations

(b) H_2 yield, energy, and H_2O conversion efficiency

Figure 5. Effect of the vapor in the absence of the catalyst.

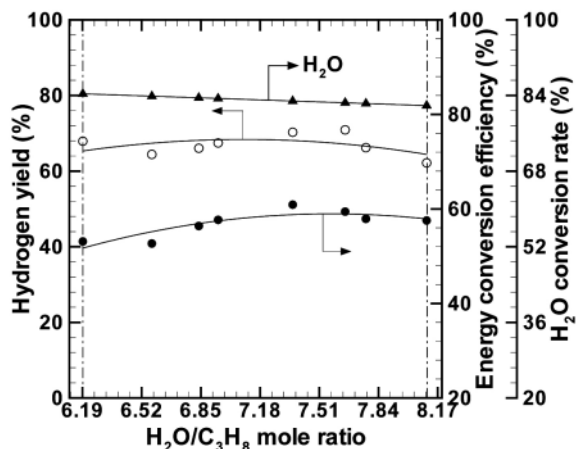(a) Selected gas concentrations

(b) H_2 yield, energy, and H_2O conversion efficiency

Figure 6. Effect of the vapor in the presence of the nickel catalyst.

action, it was found that CO was converted by reaction (4), that is, the conversion reaction of CO, and reaction (2), that is, the vapor reforming reaction. The H_2/CO ratio increased upon increasing the H_2O/C_3H_8 ratio due to the reduction of CO.

In Figure 5(b), the H_2 yield, calculated using Equation (5), was 66.3～71.2 %. H of fuel in Equation (5) was the amount of added hydrogen in the vapor. Therefore, the H_2 yield in Case V1 was lower than that in Case R. However, the conversion efficiency of H_2O gradually decreased upon increasing the H_2O/C_3H_8 mole ratio; the reforming reraction at higher H_2O/C_3H_8 mole ratio was not effective because the concentration density of C_3H_8 was low when the vapor quantity was increased. The energy conversion efficiency calculated by Equation (6) remained practically unchanged as an average value of 63.6 % with the increase of the H_2O/C_3H_8 ratio. The en-

ergy conversion efficiency of Case V1 was higher than Case R because of the increase of H_2 in the total reforming gas.

Figure 6 shows the results of the reforming reaction in which the nickel catalyst was placed in the reactor under the Case V1 experimental conditions.

In Figure 6(a), the average concentrations of H_2, CO, and CO_2 were 31.95, 6.88, and 9.73 %, respectively. The concentration of H_2 was slightly larger than it was in the absence of the catalyst (Case V1). This situation arose because nickel catalysis aided the hydrogen production reactions. However, the contents of CO and CO_2 were lower than those in Case V1 by ca. 1.4 and 0.3 %, respectively, due to increases in the residence time and adsorption.

In Figure 6(b), the average of H_2 yield was 83.06 %. The average conversion rate of H_2O was 83.06 %, less than that in Case V1. The average energy conversion ef-
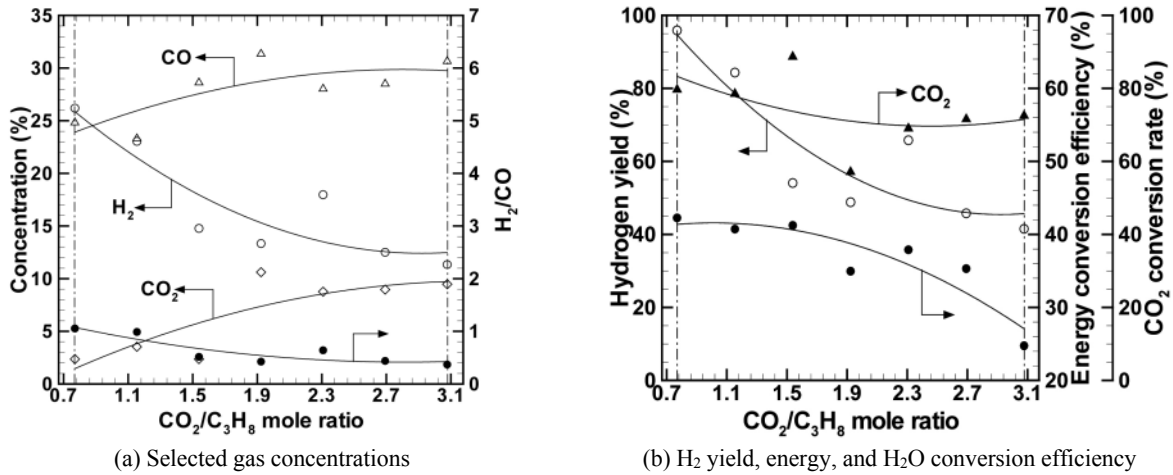
(a) Selected gas concentrations

(b) H_2 yield, energy, and H_2O conversion efficiency

Figure 7. Effect of the CO_2/C_3H_8 mole ratio.

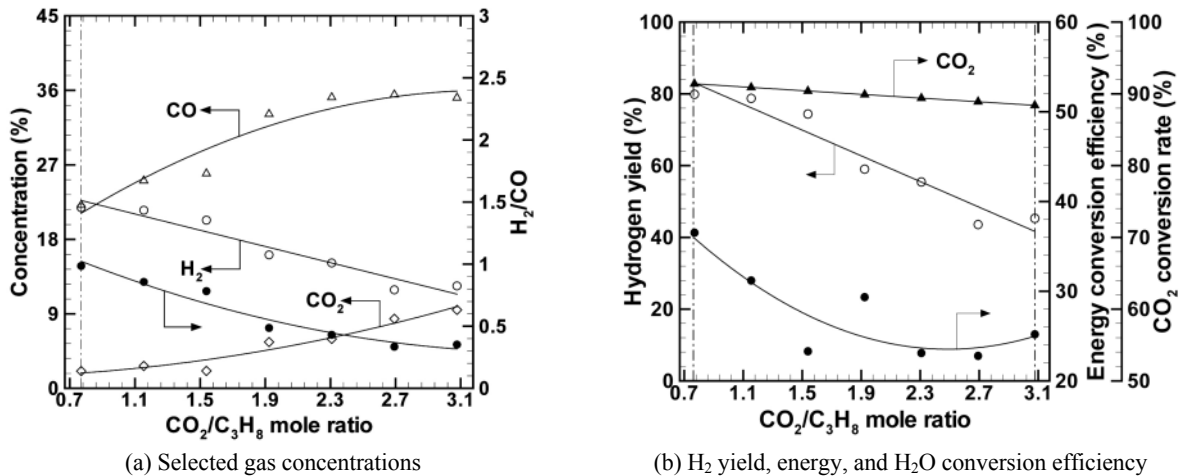(a) Selected gas concentrations

(b) H_2 yield, energy, and H_2O conversion efficiency

Figure 8. Effect of the CO_2/C_3H_8 mole ratio in the presence of the Ni Catalyst.

ficiency was 56.9 %, which was smaller than that in Case V1.

Effect of Carbon Dioxide

Figure 7 shows the result of the reforming reaction in which CO_2 was added to the standard experimental conditions of Case R.

In Figure 7(a), the concentration of H_2 (26.2～11.3 %) decreased upon increasing the CO_2/C_3H_8 mole ratio, whereas the concentrations of CO (24.8～30.7 %) and CO_2 (2.4～9.5 %) gradually increased. This result could be explained by considering that CO_2 converted to CO while H_2 was nearly unaffected. The decrease of H_2 was only due to dilution by the increased CO_2 flow rate, while the CO concentration increased drastically due to the inverse water gas shifting reaction of reaction (4) with increasing CO_2/C_3H_8 mole ratio. The H_2/CO ratio was lower than 1.

In Figure 7(b), the H_2 yield gradually decreased to 41.5

from 95.9 %. This result was expected from the concentration of H_2 in Figure 7(a). The energy conversion efficiency and CO_2 conversion rate were 42.2～24.7 % and 72.5～79.7 %, respectively. In the case of injected CO_2 a high conversion efficiency to CO was detected. However, CO was relatively smaller than the caloric value of H_2. Therefore, the energy conversion efficiency was low when compared with the other cases.

Figure 8 presents the results of the reforming reaction in which the nickel catalyst was added to the reactor under the experiment conditions of Case C1.

In Figure 8(a), the concentration of H_2 and CO were 12.4～21.82 and 22.14～35.1 %, respectively. Therefore, the H_2/CO ratio was decreased gradually. In comparison with Case C1, only the concentration of CO was detected to be higher; the concentrations of the other reforming gases exhibited comparable trends. In Figure 8(b), the H_2 yield and the energy conversion efficiency were in the ranges 45.3～79.9 and 36.5～26.1 %, respectively. The

conversion rate of CO_2 was high, in the range $88.4 \sim 91.4$ %. This result indicated that this approach is not efficient for CO_2 reforming for hydrogen production.

Conclusions

Plasma reforming was performed through partial oxidation using a plasmatron. The optimal operating conditions for producing maximum amount of hydrogen was obtained as a reference. Parametric screening studies were performed to determine the effects of vapor, carbon dioxide, and catalyst by adding H_2O, CO_2, and nickel catalyst, respectively. In the reference (Case R), the maximum values of H_2, CO, H_2/CO ratio, H_2 yield, and the energy conversion efficiency were 30.9, 20.2, 1.55, 97.7, and 40.5 % , respectively, at an O_2/C_3H_8 ratio of 1.13.

The optimal operation condition was the case of the vapor reforming (Case V1) and the vapor reforming with nickel catalyst for hydrogen production. The average value of the H_2 concentration was 32 %, higher than it was under the reference conditions (Case R). The O_2/C_3H_8 and H_2O/C_3H_8 mole ratios of the optimal operating conditions were 1.12 and 7.15, respectively.

The results of parametric studies were as follows: In the case of vapor reforming (Case V1), the concentration of H_2 remained virtually unchanged at an average value of 29.2 % upon variation of the H_2O/C_3H_8 mole ratio. However, CO was reduced as $6.6 \sim 8.6$ % by ca. 50 % in comparison with Case R. The CO_2 content and H_2/CO ratio increased upon increasing the H_2O/C_3H_8 ratio. Steam was added to the partial oxidation reforming reaction; we found that CO was converted by reaction (4), that is, the conversion reaction of CO, and reaction (2), that is, the vapor reforming reaction.

In the case of carbon dioxide, the H_2 content decreased upon increasing the CO_2/C_3H_8 mole ratio, but the concentrations of CO and CO_2 gradually increased. The H_2/CO ratio was lower than 1. This result could be explained by considering that CO_2 converted to CO through a cracking reaction, while H_2 was relatively unaffected. The decrease of H_2 was only due to dilution caused by the increased CO_2 flow rate.

In the case of reforming in the presence of the nickel catalyst, the H_2 content was slightly larger than that without catalyst. This situation arose because nickel catalysis aided the hydrogen production reactions. However, the concentrations of CO and CO_2 were lower than those in Cases V1 and C1, due to the increased residence time and adsorption.

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