저온 플라즈마를 이용한 과 수소가스 발생에 관한 실험적 연구

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Experiment study on hydrogen-rich gas generation using non-thermal plasma

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Abstract

This is a report of a feasibility study on the reduction of harmful substances such as particulate matters and nitric oxides emitted from diesel engines by using a plasma reforming system that can generate hydrogen-rich gas. In this paper, an exhaust reduction mechanism of the non-thermal plasma reaction was investigated to perform its efficiency and characteristics on producing hydrogen-rich gas. Firstly, we explain briefly the chemistry of hydrocarbon reforming. The experimental system is showed in the second part. Finally, we demonstrate the feasibility of producing hydrogen using non-thermal plasma. The experimental results are focused on the influence of the different operating parameters (air ratio, inlet flow rates, voltage) on the reformer efficiency and the composition of the produced gas.

a: air ratio
η : reformer efficiency of the reactor

1. Introduction

In order to meet the increasing concern in pollution problems from engine emission a substantial progress in engine emission control is needed. A large amount of work has been done by many scientists, which shows the possibility that the addition of relatively small quantities of hydrogen to the engine intake could result in a simultaneous reduction of both NOx and particulate emission. However, hydrogen can ignite over a wide range of air to fuel ratios and this allows leaner engine operation, thus leading to less NOx. Hydrogen combustion can also reduce hot spots, which is one of the main reasons which cause NOx emissions in internal combustion engines [1-6]. This application of Hydrogen could provide a means to reduce greenhouse gas emissions. Unfortunately, it is hard and very expensive to store pure hydrogen in a fuel engine. A small fuel reforming system that produces hydrogen-rich gas is required for utilizing hydrogen in internal combustion engine as a substantial fuel.

The plasma technology could be very attractive to reforming fuel for hydrogen production and then eliminate the pollution problems encountered in internal combustion engine emissions. The function of plasma in the reforming process is to provide the energy and to create free radical species enhancing the reaction. The catalytic effect of non-thermal plasma to produce hydrogen-rich gas in the reforming process has been demonstrated in several papers. [7-8]

A Plasma Reformer has been developed recently in our lab for hydrogen-rich gas generation using non-thermal plasma. The aim of this study was to explore the performance of this plasma device on different operational parameters. The conversion of reactants and the selectivities of products were investigated. The reforming efficiency of the system was also measured, in addition.

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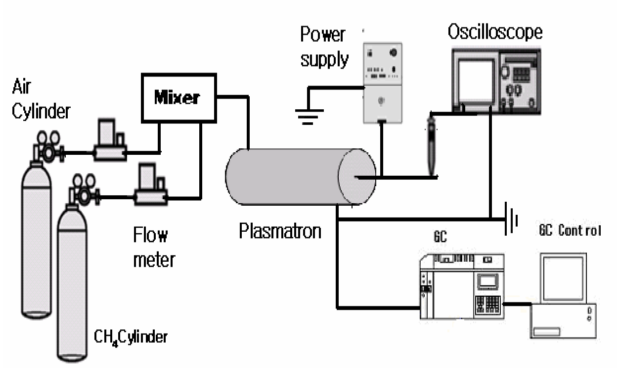

Fig. 1 Schematic diagram of experimental apparatus

2. Theoretical analysis

This part is a brief summary of the chemical reactions implied in the current plasma process.

The general idea behind reforming in the presence of air is to balance the energy required by oxidizing some of the fuel. [9] If sufficient air is added, the fuel will oxidize almost completely, yielding mainly CO_2 and H_2O. However, if the mixture is starved for air, then incomplete oxidation yields significant quantities of CO and H_2 as well, which means if we want a mixed product of rich H_2 from this chemical equilibrium, "partial oxidation" will provide a better effect.

For a general hydrocarbon fuel,

Total combustion:

$$CnHm + (n+m/4)\ O_2 \rightarrow nCO_2 + m/2\ H_2O$$

Partial oxidation:

$$CnHm + n/2\ O_2 \rightarrow nCO + m/2\ H_2$$

The partial oxidation step requires n/2 moles of O_2 to shift each mole of fuel.

In case of methane, the quantity of air injected in the reactor is defined using the air ratio a. The air ratio corresponds to the ration between the amount of injected oxygen coming from air and the amount of oxygen needed for a total combustion of methane.

Total combustion: $CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$

Partial oxidation: $CH_4 + bO_2 \rightarrow c\ CO + d\ H_2$

The air ratio is then defined as: a=b/2

Table 1 Operation conditions of the plasma reformer

Fuel	Methane
Input power supply voltage	8—25kV
Oxidants	Air
Feed flowrate	20—400 cm^3/min

CH_4, molar mass: 16.04 g/mol; LHV=32.9 KJ/L; HHV=36.5 KJ/L

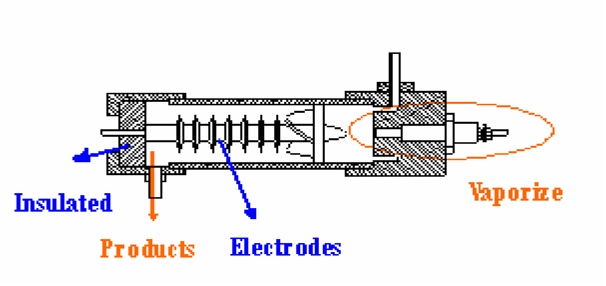

Fig. 2 Schematic diagram of plasmatron

The conversion of either methane or oxygen in this reforming process is defined as

$$\text{Conversion (CH}_4\text{)} = \frac{X_{CH_4} - Y_{CH_4}}{X_{CH_4}} * 100\%$$

$$\text{Conversion (O}_2\text{)} = \frac{X_{O_2} - Y_{O_2}}{X_{O_2}} * 100\%$$

where X and Y denote the mole of reactants in and out.

The selectivities of products containing carbon atom are calculated based on carbon balance, whereas the selectivity of hydrogen is determined from hydrogen balance as follows:

$$\text{Selectivity (CnHm)} = \frac{Z_C}{W_C} * 100\%$$

$$\text{Selectivity (H}_2\text{)} = \frac{Z_H}{W_H} * 100\%$$

where Z and W denote the mole of products and total consume.

The reformer efficiency is defined as the energy present in hydrogen at the output of the reactor versus the input energy coming from methane. The reformer efficiency is then calculated with the following relation:

$$\eta = \frac{(n_{CO} + n_{H_2})\Delta H_{H_2}}{n_{CH_4}\Delta H_{CH_4} + P}$$

where n_{CO} and n_{H_2} denote the mole flux of carbon monoxide and hydrogen emitted from the plasma reactor, n_{CH_4} denotes the input methane flux. ΔH_{H_2} and ΔH_{CH_4} denote the lower heat of combustion for hydrogen and methane. P, the electric power provided to the gas by the plasma discharge.

3. Experiment

3.1 The experiment set-up

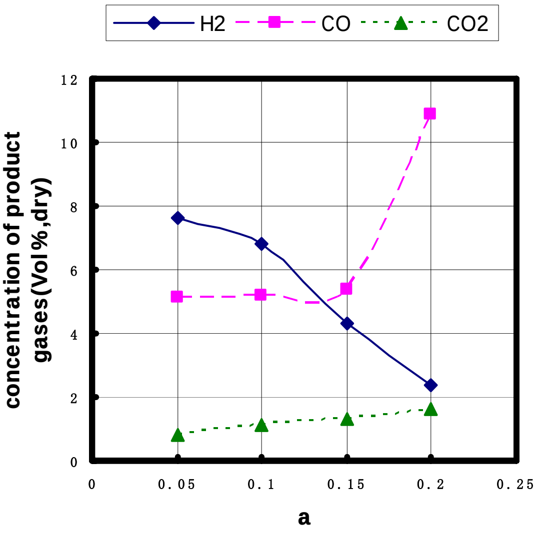

Fig. 3 Composition/Air ratio

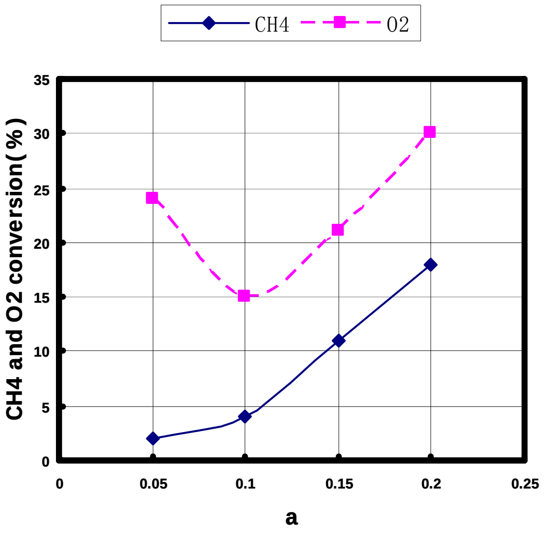

Fig. 4 Conversion/Air ratio

The schematic diagram of this reforming system is presented in Figure 1. The system is composed of a plasmatron as a reactor, two flow meters to control the flowrate of air and methane, a high voltage discharge power supply, and a gas chromatograph. Air is used as reforming gas and methane is used for reformation. The whole system is set up wherein air and vaporized methane are mixed at a desired ratio and injected into the plasmatron by an atomizer. After treatment the hydrogen-rich sample gases emitted were analyzed using GC. Each time before use, this GC was calibrated for five minutes with atmospheric air.

3.2 The experimental conditions

The plasma reformer presented in this study has been designed to work with non-thermal plasma. The working specifications of the plasma reformer are summarized in Table 1. Input voltage from power supply is up to 25kV. The flowrates of methane and hydrogen inputted to the reactor are up to 400 cm^3/min (Table 1).

3.3 The plasmatron

The function of using plasma is to play a catalytic role by creating reactive species needed for the chemical reactions [10]. A plasmatron is a device based on the principle of arc plasma that can heat the gases to very high temperatures at which the gas is partially ionized.

The plasmatron presented in this study is composed of a stainless-steel vessel, an electrode and a vaporizer. The stainless-steel vessel is connected with the high voltage power supply at one side and the ground at another side. Air and methane are mixed before entering the plasmatron and injected via a stainless-steel tube. The reactants are then vaporized before starting the reaction in the plasmatron. Arc discharge arises between the cathode and the anode through the space in which the charge material is contained when the high voltage power supply working. Methane is oxidized then. Reformed gas comes out (Fig. 2).

4. Results and discussion

The characteristics of plasma reforming of methane and air mixtures have been simulated for conditions close to those experiments [10-11]

4.1 Effects of air ratio

Fig. 3~6 show the evolution of the concentration of the different products, the conversion of CH_4 and O_2, the selectivity of products and the reformer efficiency of this plasmatron fuel reforming system as a function of air ratio under a condition of flow rate equals to 200cm^3/min and voltage equals to 17500V. The total air ratio is maintained in this study at 0.25.

The evolution of concentration-to-air ratio is shown in Fig. 3. The maximum hydrogen yield is obtained for an air ratio equals to 0.05. Meanwhile, the minimum carbon monoxide and carbon dioxide yield are produced. The concentration of hydrogen yield decreases as the air ratio increases. This is due to the dilution effect of nitrogen in air, which is used as oxidant. The highest amount of carbon monoxide and carbon dioxide were observed at a 0.2 air ratio. This is mainly explained the reason that an increase in the air ratio results in having more oxygen available to react with methane molecules, which leads to higher conversion of CH_4 and O_2 of 18% and 30% (corresponding to 0.2 air ratio), Fig.4.

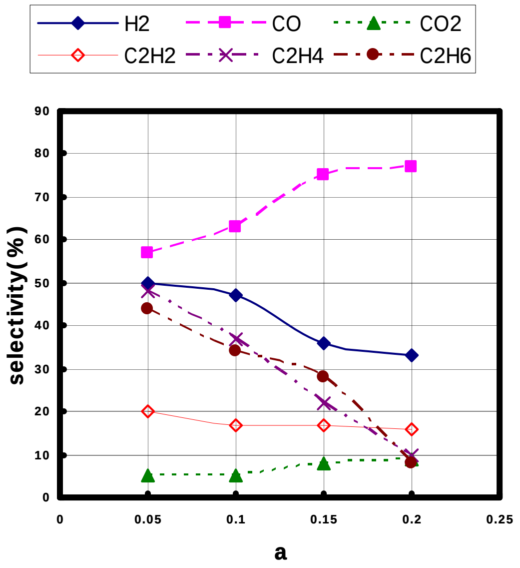

Fig.5 Selectivity/Air ratio

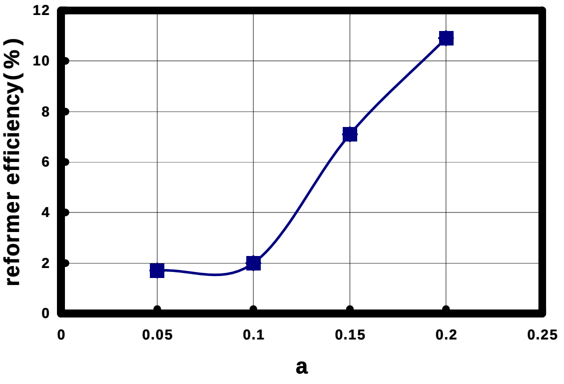

Fig. 6 Reformer efficiency/Air ratio

The variation of the selectivity of the chemical species with air ratio is shown in Fig. 5. There is an evidently decrease from 50% to 33% of hydrogen selectivity with increasing the air ratio from 0.05 to 0.2, whereas both CO and CO_2 selectivities increases slightly. The selectivities of C_2H_2, C_2H_4, C_2H_6 reaches 20%, 48%, 44% at a 0.05 air ratio and reduces to 16%, 10%, and 8% at a 0.2 air ratio. It can be explained due to the increase of air ratio (more oxygen available) causes the dimerization of active methane species reacting with another one to form C_xH_y products has less opportunity than the methane oxidation to form CO_x.

Fig. 6 shows the variation of the reforming efficiency of this plasmatron fuel reforming system. The reformer efficiency shifts with the same tendency as the concentration of carbon monoxide (Fig. 3), that is, the increment from 1.7% to 10.9% corresponding to an increment of air ratio from 0.05 to 0.2.

4.2 Effects of inlet flow rates

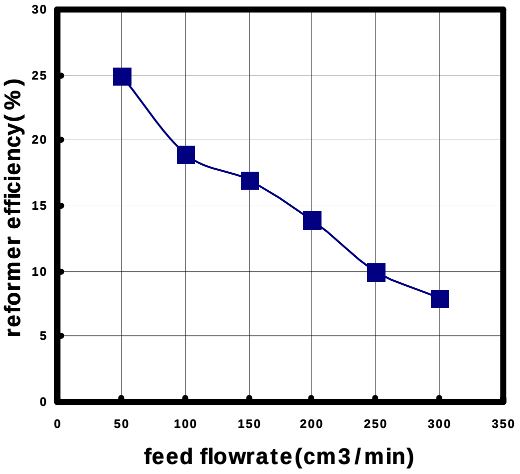

Fig. 7 Reformer efficiency/Feed flowrate

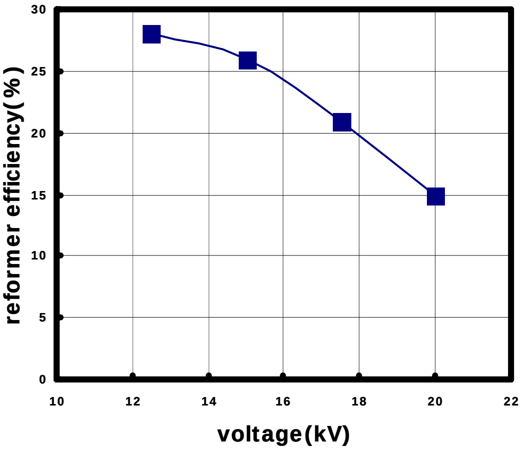

Fig. 8 Reformer efficiency/Voltage

The movement of reformer efficiency is shown in Fig. 7 according to the increase of feed flowrate under a certain condition (air ratio, 0.1; voltage, 17500V). The reforming efficiency is decreasing with increasing feed flowrate. Increasing feed flowrate reduces the resident time of gas inside the reactor and the chance for CO_2 to collide with electron or other exited species in the plasma reaction.

4.3 Effects of voltage

The effect of voltage on the reformer efficiency of this plasmatron reforming system is illustrated in Fig.8 (air ratio, 0.1; feed flowrate, 200 cm^3/min). The results indicated that the reformer efficiency decreases drastically as the power increases. This is especially due to the fact that the increasing of fuel power increases the inlet velocities of the gas and then decreases the resident time of the gas in the plasma reactor.

5. Conclusions

Plasmatron fuel converter technology consists in the use of a plasma discharge for the initiation of reformation process. The increased ionization levels and mixture of gas and fuel accelerate reformation of hydrocarbon fuels into hydrogen-rich gas.

The plasmatron presented in this study can operate at atmospheric pressure, with air as the plasma forming gas. The basic characteristics of this plasma reformer are investigated by experimental results for the generation of hydrogen-rich gas. The development of dissociation of methane due to discharge under several conditions has experimentally been observed. Experimental analyses are performed in order to optimize the design of the plasma reformer and to confirm the influence of plasma conditions on hydrogen production.

The concentration of hydrogen decreases substantially with increasing air ratio in reaction, since the dilution effect of nitrogen in air, which is used as oxidant. The conversion of CH_4 and O_2 increases with increasing air ratio, for the reason that an increase in the air ratio results in having more oxygen available in reaction. The selectivity of hydrogen decreases and the reformer efficiency increases with increasing air ratio. A higher feed flowrate and voltage decreases the reformer efficiency since a reduction of resident time of gas inside the reactor. The results indicate that the optimum conditions of this system are a 0.1 air ratio, a feed flowrate of 200 cm^3/min and a voltage of 17500V.

The next step of this study will be thus focused on the following points:

- Improvement of the plasma reactor.
- The effect of increasing the operating temperature, frequency, current and pressure on the reformer efficiency.
- To input fuel instead of methane as reactant.

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