[20a]

Development of Liquid Fuel Reformer Using Low Energy Pulse (LEP) Discharge at Room Temperature

Yasushi Sekine, Masahiko Matsukata, Eiichi Kikuchi, Shigeru Kado
Waseda Univ. 55S602, Okubo, Shinjyuku Tokyo, 169-8555 Japan
Phone: +81-3-5286-3114
Fax: +81-3-5286-3114
Email: yasushisekine@mac.com

Abstract

We studied steam reforming of ethanol at room temperature and atmospheric pressure using low energy pulse (LEP) discharge. In this study, we employed characteristic novel reformer, one electrode was made of carbon fibers (o.d. 7.0 μm) bundle. So fuel was supplied to discharge region by capillary action of the fibers and reformed directly by LEP plasma without any pump or heater. When using this reformer, at first, the fuel was evaporated by heat emission from electrode, and then the vaporized reactants were reacted. Produced gaseous compounds were collected from upper part of the reactor, and analyzed by gas chromatography. H_2 and other compounds: CO, CH_4, CO_2, C_2H_4, and C_2H_6 were produced, and the formation rates were increased in proportion to the increase of the gap distance and input power. And compared to the former conventional reformer, the results were equivalent to the rates of gas phase reactor. The effects of ethanol concentration and of energy efficiency were studied, and the energy efficiency (LHV based) has reached 89.3 % at the ethanol concentration of 50 %, the discharge gap of 3.0 mm.

Introduction

Recently fuel cell is attracting attention. Especially, Polymer Electrolyte Membrane Fuel Cell (PEMFC) is one of the candidates. Because it is operated lower temperature than that of other fuel cell, and it has high performance in energy efficiency. Other reasons, clean exhaust gases, small size, light weight, fast start-up, rapid response and so on are also worthy of remark. So PEMFC is expected to serve as a fuel cell vehicle (FCV) and a home cogeneration system. But recent considerable Hydrogen production and transportation processes have many problems with the present technology (for example, The transportation and storage of Hydrogen), so it is need to research innovative technological methods to produce Hydrogen. So, we applied low energy pulse (LEP) discharge for this purpose. If LEP discharge used for reforming, reactions can be achieved at room

temperature and atmospheric pressure. On the other hand, ethanol has a potential for being an alternative fuel replacing fossil fuels because ethanol can be produced from various renewable sources. So we tried to unify a supply and storage system with using liquid fuel (ethanol and water solution) and LEP discharge. And it was also attempted to design much smaller reformer, and improve energy efficiency.

Experimental

Fig. 1-(a) shows our previous fuel delivery system. No catalyst was used, and Ar was used as a carrier gas. Gap distance of electrodes was fixed at 2.1 mm. Our previous reformer was flow type reactor, and the mixture of ethanol and water was supplied by chemical pump, and evaporated at 413 K. The reaction temperature was set at 393 K to prevent condensation into liquid.

On the other side, Fig. 1-(b) shows our novel system. The bottom of carbon fiber bundle was soaked into ethanol solution contained in a small bottle. Present reformer was so attractive, because it was no need of heaters or pumps at all. This reformer used carbon fiber bundle as electrode. The solution could be pumped up to the top of the carbon fiber bundle by capillary action and supplied into discharge region.
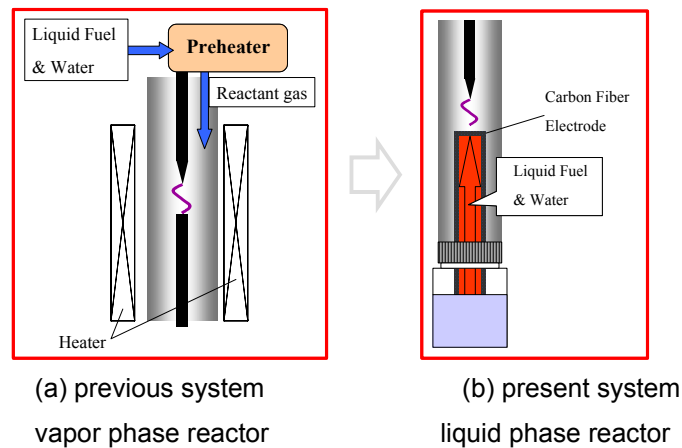

(a) previous system
vapor phase reactor

(b) present system
liquid phase reactor

Fig. 1 Schematic diagram of previous and present fuel delivery system to discharge region.

And, liquid fuel was evaporated by Joule heat which generate from internal resistance of electrode. The supplied fuel amount was controlled by the length and number of carbon fibers. The amount became larger in proportion to fiber length and fiber number. And the supplying fuel amount into the discharge region was about 30 cc min^{-1}, when the length was 7 cm and the number of carbon fiber was 84,000.

And a DC power supply (Matsusada precision inc. HARb-40R30) was used to produce the non-equilibrium pulsed discharge. All products were analyzed using a gas chromatography equipped with FID and TCD (Shimadzu GC14-B). The waveforms of current and voltage were observed by a digital signal oscilloscope (DSO):(Lecroy 9314C).

Results and Discussion

1) Comparison of the vapor phase reaction and the liquid phase reaction

Here, steam reforming of ethanol proceeded and hydrogen obtained as a main product. In addition to hydrogen, gases such as carbon monoxide, carbon dioxide, C2 compounds (mainly acetylene) and methane were produced. And the amount of produced gas increased in proportion to the increase of the gap distance of electrodes. But there is no influence of the gap distance of electrodes on the selectivity to product. So we discussed difference of H_2 formation rate before and after improvement. It was shown in Fig. 2. They showed almost same trends. So the discharge energy loss in case of vapor phase reactor was partly utilized to vaporize ethanol solution in the case of liquid phase reactor. Moreover, it was possible to lessen the size of the reformer compact, and make the process more efficient, because of the needless to install such equipments as heaters to evaporate liquid fuel.
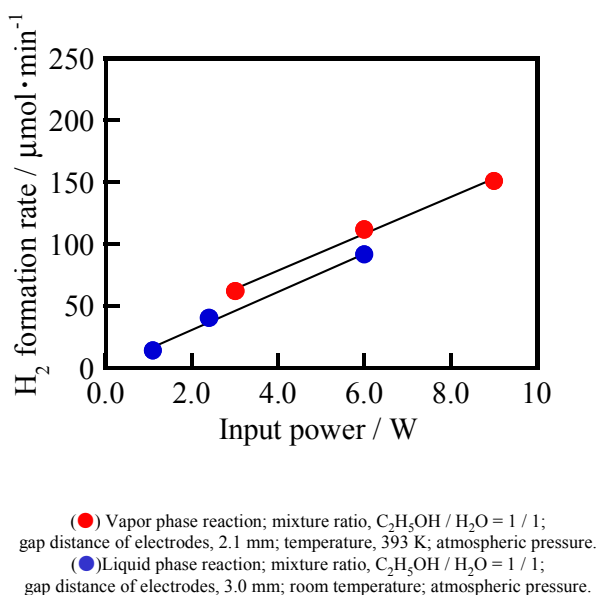

($\bullet$) Vapor phase reaction; mixture ratio, C_2H_5OH / H_2O = 1 / 1;
gap distance of electrodes, 2.1 mm; temperature, 393 K; atmospheric pressure.
($\bullet$)Liquid phase reaction; mixture ratio, C_2H_5OH / H_2O = 1 / 1;
gap distance of electrodes, 3.0 mm; room temperature; atmospheric pressure.

Fig. 2. Comparison of previous and present reaction system

2) Effect of input power

In this section, we investigated effect of input power on ethanol consumption rate and carbon selectivity. The results of ethanol consumption rate and carbon selectivity are plotted

against the input power in Fig. 3. As shown in Fig. 3, carbon selectivity was almost stable under any conditions.
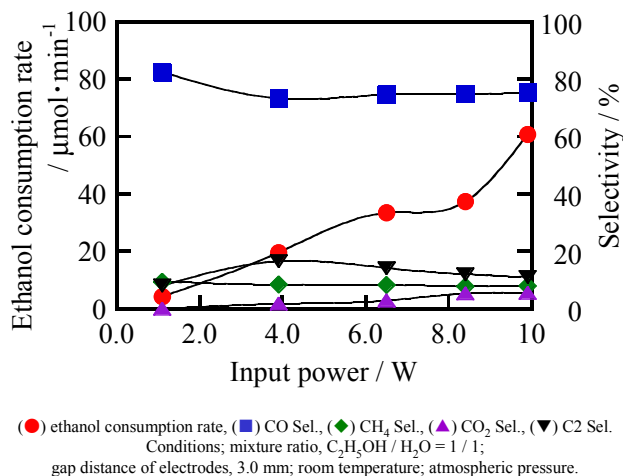

($\bullet$) ethanol consumption rate, ($\blacksquare$) CO Sel., ($\blacklozenge$) CH_4 Sel., ($\blacktriangle$) CO_2 Sel., ($\blacktriangledown$) C2 Sel.
Conditions; mixture ratio, C_2H_5OH / H_2O = 1 / 1;
gap distance of electrodes, 3.0 mm; room temperature; atmospheric pressure.

Fig. 3. Effect of input power on ethanol consumption rate and on Carbon selectivity.

3) Effect of concentration of C_2H_5OH and H_2O

In this section, we investigated effect of concentration of ethanol and water. At first, H_2 and O_2 were not generated when H_2O concentration was 100 %. So the reaction of water electrolysis did not advance. Next, at the decomposition reaction of ethanol 100 %, small amount of carbon deposition were gradually formed, and it caused destabilization to stop the discharge. So the discharge couldn't be kept stable for a long time. On the other hand, when the reaction was handled in the case of steam reforming (0 < ethanol concentration < 100), the discharge could be stabilized for a long time and could be continued in steam reforming without stopping the reaction.
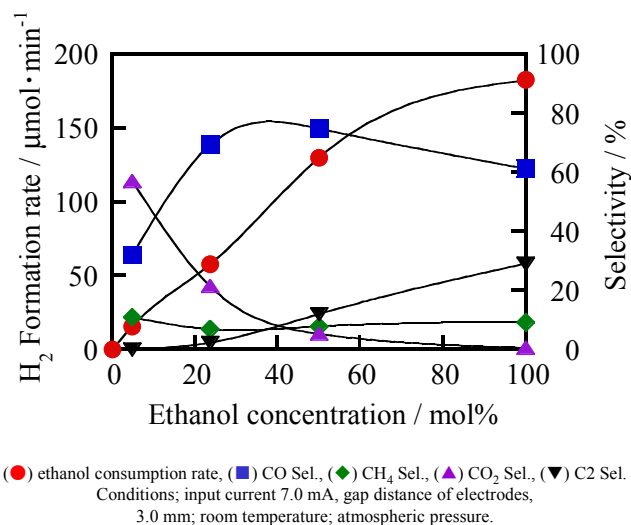

($\bullet$) ethanol consumption rate, ($\blacksquare$) CO Sel., ($\blacklozenge$) CH_4 Sel., ($\blacktriangle$) CO_2 Sel., ($\blacktriangledown$) C2 Sel.
Conditions; input current 7.0 mA, gap distance of electrodes,
3.0 mm; room temperature; atmospheric pressure.

Fig. 4. Effect of ethanol concentration on H$_2$ formation rate and on Carbon selectivity.

Fig. 4 showed the results. The larger ethanol concentration is, the more produced H$_2$. And higher ethanol concentration field, C2 selectivity was rather high (it was about 30 %), compared to that of lower ethanol concentration field. So it seems to say that the reaction of which ethanol concentration is from 20 to 50 mol% is the highest efficiency at a present stage. Because C2 selectivity was not high, and carbon deposition was not observed.

4) Calculating result of Energy efficiency

Input power was regarded as the power consumption in the discharging space. And it was calculated from integration value which is current multiply by voltage, picked up from the waveforms of the oscilloscope. Here, input power (Ei) was calculated based on the following formula.

$$Ei = \sum_t \{(v_i + v_{i+1})/2\} \times \{(c_i + c_{i+1})/2\} \times (t_{i+1} - t) \times f \tag{1}$$

On the other hand, output power was regarded as the difference of the standard enthalpy of formation between the amount of liquid fuel converted and the amount of compounds formed. Finally energy efficiency was calculated based on LHV as shown in Table 1.

Table 1   Energy efficiency calculation based on LHV

Formula	Formation/Consumption [mmol/min]	Q_{LHV} [MJ/mol]	E_{LHV} [kJ/min]
C_2H_5OH	0.10	1.36	0.129
H_2O		0.00	0.000
Electricity	(0.25W)		0.015
		E_{input}	0.144
H_2	0.24	0.24	0.058
CO	0.10	0.28	0.028
CH_4	0.02	0.80	0.016
CO_2	0.03	0.00	0.000
$C_2H_X{}^*$	0.02	1.32	0.026
		E_{output}	0.129
	Energy efficiency based on LHV		89.3%

* X=2, 4 and 6, Q is average among 2 to 6

Conditions; ambient temperature, atmospheric pressure

And, its energy efficiency reached up to 89% at LHV (Lower Heating Value) based calculation at the ethanol concentration of 50 %, the gap distance of electrode 3.0 mm. The efficiency in this experiment was exceeding that of the former way. Furthermore, this reformer has a potential to improve the efficiency by controlling voltage and current system.

Fig. 5   Photo for live novel model

CONCLUSIONS

We succeeded in improving the energy efficiency because the liquid phase reactor does not require a heater which is needed to vaporize the mixture of water and ethanol. Moreover any pump supplying the liquid into the reactor was not required. So the liquid phase reactor made the process scale reduced, and also made the device size compact without spoiling its function. Therefore, if the controlling voltage and current system makes more progress, we consider that this process would be very useful for room temperature hydrogen formation system.

REFERENCES

(1) Kado, S., Y. Sekine and K. Fujimoto, ; "Direct synthesis of acetylene from methane by direct current pulse discharge" Chem Commun., 1999, 24 2485.

(2) Kado, S., K. Urasaki, Y. Sekine and K. Fujimoto, ; " Low temperature reforming of

methane to synthesis gas with direct current pulse discharge method" Chem. Commun., 2001, 5 415.

(3) Martin K., B. Eliasson, U. Kogelschatz and A. Wokaun,; " CO2 reforming of methane by the combianation of dielectric-barrier discharge and catalysis," Phys. Chem. Chem. Phys., 2001, 3, 294-300.

(4) Nozaki, T., Y. Miyazaki, Y. Unno and K. Okazaki, ; "Energy distribution and heat transfer mechanisms in atmospheric pressure non-equilibrium plasmas" J. Phys. D: Appl. Phys. 34 (2001) 3383-3390.

(5) Nozaki, T., Y. Unno and K. Okazaki, ; "Thermal structure of atmospheric pressure non-equilibrium Plasmas" Plasma Source Sci. Technol. 11 (2002) 431-438.

(6) Sekine, Y., K. Urasaki, S. Kado, M. Matsukata, and E. kikuchi, ; " Nonequilibrium Pulsed Discharge: A Novel Method for Steam Reforming of Hydrocarbons or Alcohols" Energy Fuels, 2004, 18, 455-459.

(7) S.L. Yao, M. Okumoto, A.Nakayakma and E. Suzuki, ; " Influence of Rise Time of Pulse Voltage on the Pulsed Plasma Conversion of Methane," Energy Fuels, 2001,15,1295.

(8) Wonihl C., Y. beak, S. Moon, Y. C. Kim, ; "Oxidative coupling of methane with microwave and RF plasma catalytic reaction over transitional metals loaded on ZSM-5," Catal. Today 74 (2002) 207-223.