Hydrogen Production from Biomass-Ethanol at Ambient Temperature with Novel Diaphragm Reactor

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We used a novel liquid-fuel-reforming system, with a diaphragm and discharge hybrid apparatus that can be operated under ambient temperature and atmospheric pressure, to obtain 50% hydrogen by steam reforming of ethanol with high energy efficiency of up to 95%.

Recently, fuel cells have attracted remarkable attention. Polymer electrolyte membrane fuel cells (PEMFCs) can be operated at lower temperature than other fuel cells. They offer particularly high energy efficiency. Their other features include clean exhaust gases, small size, light weight, fast start-up, rapid response, and so on. For those reasons PEMFC is anticipated for application in fuel cell vehicles (FCVs) and home cogeneration systems. So far, recent considerable hydrogen production and transportation processes are hindered by numerous obstacles including the transportation and storage of hydrogen. Innovative technologies for hydrogen production and storage must be developed. Recently, we postulate that low energy pulse (LEP) discharge is a candidate to solve those problems.[1–7] This technique's reactions occur at room temperature and atmospheric pressure if LEP discharge is applied for reforming. On the other hand, ethanol is an alternative fuel to replace fossil fuels because ethanol can be produced from various renewable sources. Therefore, we try to unify a provision and storage system using liquid fuel (an ethanol–water mixture) and discharge.

Diaphragm discharge is a new kind of liquid-phase discharge at ambient temperature and atmospheric pressure.[8,9] An outline image of the reactor and experimental apparatus are shown in Figure 1. Figure 1 also shows that a pair of electrodes are set in the liquid fuel. A diaphragm membrane with a 0.25–2.0-mm diameter pinhole is inserted in the middle of the reactor. This membrane has an important role for this discharge. The diaphragm centralizes electrons in the pinhole, thereby generating a liquid-phase discharge that facilitates liquid-phase reforming.

In this study, an ethanol–water mixture was chosen as a target fuel. The electrode gap was fixed at 6.0 mm. A DC power supply (Matsusada Precision Inc.) produced the nonequilibrium pulsed discharge. All products were analyzed using a gas chromatograph equipped with FID and TCD (GC14-B; Shimadzu Corp.) The waveforms of current and voltage were observed using a high voltage probe, a current probe, and a digital phosphor oscilloscope (DPO; Tektronix Inc.) In any cases, the input power of discharge was controlled by the input current. The voltage in the steady state was about 4–7 kV and it depended on conditions like the diameter of pinhole.

First, we examined the diaphragm role in this discharge. Results with and without the diaphragm were compared. After the reaction without a diaphragm, the electrode was corroded and

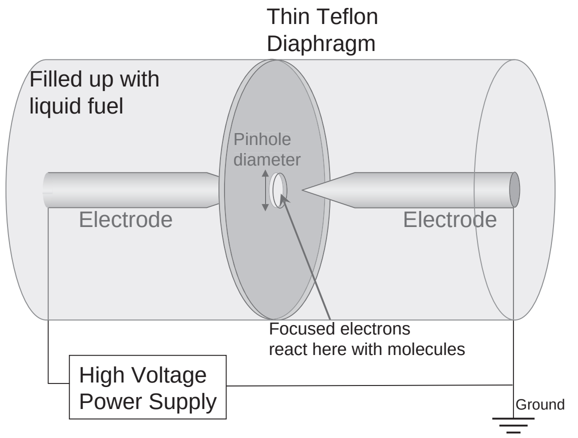

Figure 1. Outline for the diaphragm discharge apparatus.

discharge stopped soon after the reaction started. It was considered that the diaphragm pinhole allowed electrons to move from cathode to anode, whereas ions and molecules were hardly allowed by the small pinhole (<ca. 0.5 mm). Thereby, the diaphragm pinhole controlled mass transfer and ionic reaction caused by electrolysis. On the other hand, it turns out that the electrodes were very stable with a diaphragm. Consequently, discharge continued stably for a long time.

Next, we investigated the correlation between shapes of electrodes and yield of products. Figure 2 shows that shapes of electrodes had a remarkable influence on the gas yield in this reaction. The discharge showed the highest formation rate and hydrogen and carbon monoxide generated predominantly when using a couple of coaxial needle type of electrodes (Type A).

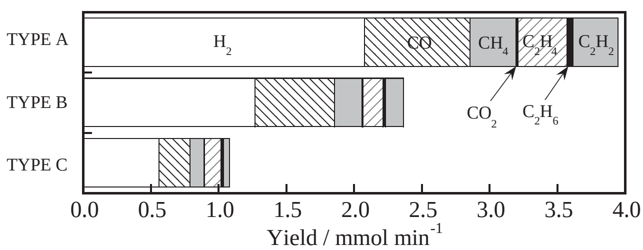

Figure 2. Effect of shapes of electrodes on gaseous product formation in diaphragm discharge: Type A; needle to needle shapes; Type B; needle to plate (ground side) shapes; Type C; plate to needle (ground side) shapes. Conditions: discharge gap, 6.0 mm; C_2H_5OH concentration, 50 mol %; pinhole diameter, 1.0 mm; input current, 15.0 mA; diaphragm thickness, 1.0 mm.

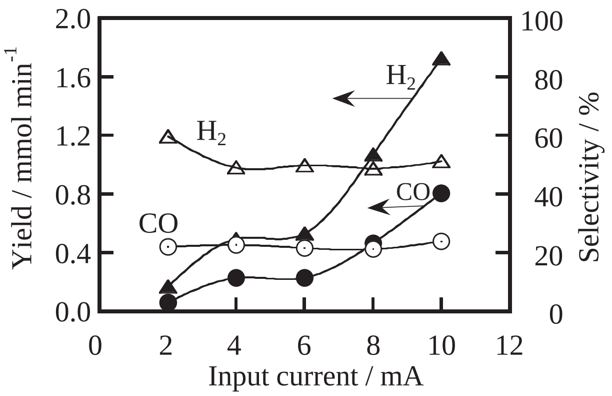

Figure 3. Effect of input current on yield of gaseous products and on carbon selectivity. Conditions: discharge gap, 6.0 mm; C_2H_5OH concentration, 50 mol %; pinhole diameter, 0.5 mm; diaphragm thickness, 1.0 mm.

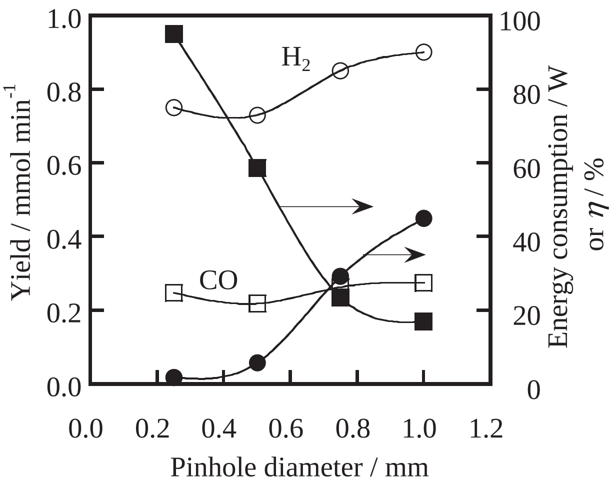

Figure 4. Effect of pinhole diameter on yield of gaseous products, energy consumption, and efficiency: ●, energy consumption; ■, energy efficiency (η). Conditions: discharge gap, 6.0 mm; C_2H_5OH concentration, 50 mol %; input current, 7.0 mA; diaphragm thickness, 1.0 mm.

That phenomenon was similar to selectivity in a vapor-phase reaction. The couple of coaxial needle type of electrodes was selected in the following experiments. On the other hand, diaphragm discharge with a pair of flat plate and needle electrodes (Type B and Type C) was very difficult to control and the discharge was not stable. The effect of input power on gaseous products yield was also examined, the result is shown in Figure 3. This result shows the same trend (more gas is produced with greater input power) as the gas-phase reaction performed previously. Therefore, it was also proved that the number of electrons at the gap of electrodes serves as an important factor in this liquid-phase discharge. The effect of diameter on the diaphragm pinhole was also an important factor in this discharge. Figure 4 shows the results. Very high power was required when the pinhole diameter was large. Focusing electrons on the pinhole was important, but too small pinhole would be damaged immediately by the discharge. Therefore, the optimal pinhole diameter was inferred to be between 0.25 and 0.5 mm. We also examined the diaphragm thickness effect, but it showed no change. The important element in this discharge was not the focused electron volume, but the focused electron density.

Energy efficiency (η) based on the lower heating value (LHV) was calculated using the following formula

$$\text{Energy efficiency } (\eta) = (\Sigma E_{\text{output}}/\Sigma E_{\text{input}})^{*}100. \qquad (1)$$

Maximum efficiency achieved in this study was 95% (Figure 4). The key point for this discharge is the manner of focusing the electrons.

Using the diaphragm membrane, liquid-phase discharge succeeded at ambient temperature and atmospheric pressure. The main gas obtained was hydrogen. The amount of produced gas increased in proportion to the increase of input current. It showed similar trends to that of vapor-phase discharge. In the liquid phase, trace amounts of by-products were observed after long period of reaction but it was difficult to identify them. In this discharge, the most important factor was the diaphragm pinhole diameter; in other words, it was important to focus electrons on the microscopic pinhole. The maximum efficiency in this discharge was 95%. In addition, this reformer is anticipated for use in future hydrogen-manufacturing proceses because the reformer is very simple. This novel reformer is attractive because the liquid-phase reactor needs no heater to vaporize the ethanol–water mixture and prevent its condensation. Moreover, no pump is required to transport the liquid into the reactor. Consequently, the process scale is reduced drastically. This liquid-phase reactor has another merit: outlet gas does not include unreacted ethanol, which is usually included except for 100% conversion rate in the case of a vapor-phase reactor. We have thus produced a very simple and small reformer.

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