

## 유기성 폐기물 및 폐수로부터 2단계 생물학적 수소생산 및 통합화 시스템

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## Two-stage Biological Hydrogen Production from Organic Wastes and Waste-waters and its Integrated System

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### ABSTRACT

유기성 폐기물을 이용하여 생물학적 수소생산 통합화 시스템 연구를 수행하였다. 통합화 시스템은 유기성폐기물의 전처리, 2단계 혐기발효 및 광합성 배양으로 구성된 생물학적 수소생산 공정, 초임계수 가스화 공정, 생산된 가스의 저장, 분리 및 연료전지를 이용한 전력 생산으로 구성되었다. 실험에 사용된 유기성 폐자원은 식품공장 폐수, 과일폐기물, 하수슬러지이며, 전처리는 폐기물에 따라 열처리 및 물리적 처리를 하였으며, 전처리된 시료는 생물학적 수소생산 공정에 직접 적용되었다. *Clostridium butyricum* 및 메탄 생성조에서 발생하는 하수슬러지중의 미생물 복합체는 수소생산 혐기 발효공정에 사용되었으며, 광합성 수소생산 미생물인 홍색 비유황 세균은 광합성 배양에 사용되었다.

생물학적 공정에서 발생하는 미생물 슬러지는 초임계수 가스화 공정으로 수소를 발생하였으며, 슬러지 중의 COD를 저하시켰다. 생물학적 공정 및 초임계수 가스화 공정에서 발생하는 수소는 가스탱크에 가입상태로 저장한 후, 95%순도로 분리하였으며, 정제된 수소는 연료전지에 연결하여 전력생산을 하였다.

**주요기술용어** : Bio-hydrogen(생물학적 수소), Purple non-sulfur bacteria(홍색 비유황세균), Photosynthetic cultivation(광합성 배양), Anaerobic fermentation(혐기 발효), Organic wastes(유기성 폐기물), Integration(통합화)

# 1. Introduction

Due to the limited landfill area and the typical diet pattern of high moisture contents meal in far-east Asia, disposal of organic wastes and wastewater is one of the major environmental problems causing surface and ground water pollution, etc<sup>1-3)</sup>. Biological hydrogen production has often been under-evaluated in terms of environmental aspects because the effluents produced during the process has excess microbial cell population, which has an associated disposal cost. However, Biological hydrogen production using biomass can accomplish two goals simultaneously, the clean energy production and the organic waste treatment. Therefore, an integrated system was developed for the biological hydrogen production from biomass. In conjunction with the biological process, a supercritical water gasification process<sup>4)</sup> was also used in this research to produce hydrogen from the microbial sludge which was the outflow from the biological process (see Fig. 1). The hydrogen gas was purified from the mixture of gases produced, stored and used to generate electrical power using fuel cells.

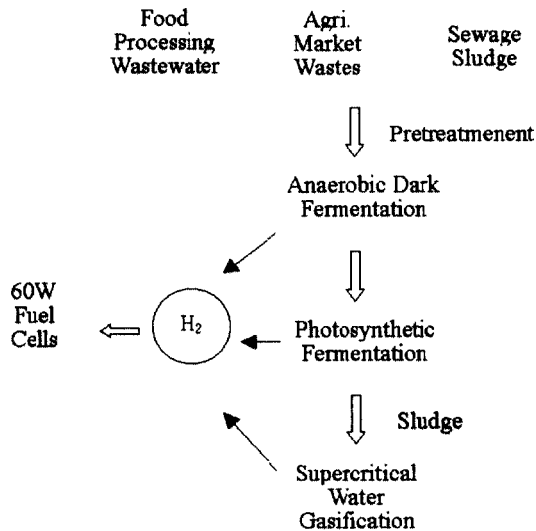


Fig. 1. Overview of an integrated system of hydrogen production.

municipal wastewaters treatment plant in Daejeon, Korea.

## 2.2 Analysis

BOD, COD, total solids, suspended solids, and volatile solids were determined by standard methods<sup>5)</sup>. Sugar contents were measured by the dinitrosalicylic acid (DNS) method<sup>6)</sup>. Soluble starch contents were determined by the DNS method after acid hydrolysis using 5.5 N HCl. The concentration of organic acids was measured using Beckman gold model 420 high performance liquid chromatography fitted with a Aminex HPX-87H (Bio-Rad) organic acid analysis column and using Shimadzu 14-B gas chromatography equipped with a flame ionization detector after the sample was pre-treated with HCl. The column was packed with Porapak QS and nitrogen was used as a carrier gas. NH<sub>3</sub>-N contents were estimated

## 2. Materials and Methods

### 2.1 Wastes and wastewater

Organic waste and wastewaters used in this research were watermelons, mandarins and apples collected from the local agricultural market during their seasons. Traditional rice wine (Makkolii) and Tofu wastewaters were also collected from local manufacturing factories and sewage sludge from the

using an ammonia electrode (Corning) equipped with an ion/pH meter.

### 2.3 Immobilization of bacteria

*R. sphaeroides* E15-1 was obtained from Bae et al.<sup>7)</sup> It was cultured with 12g of hydrophilic cuprammonium rayon hollow fibers (diameter x length, 180  $\mu$ m x 3Cm) in the modified Ormerod media for 2 months at 30-32°C under 154  $\mu$ M photon/m<sup>2</sup>/sec irradiance using tungsten halogen lamps. Culture media was changed every week and flushed with oxygen-free argon.

### 2.4 Pretreatment of sewage sludge

Sewage sludge was pre-treated for 1 h at 150°C under 10 atm after the pH was adjusted to 14 with NaOH. Ammonia in the gas phase was vented at 70-80°C after heat-treatment and 3-4 L of sewage sludge was processed in a 7 L reactor.

### 2.5 Hydrogen production

*Cl. butyricum* NCIB 9576 was anaerobically precultured in PYG synthetic media containing 1% glucose for 24 h at 37°C after flushing the flask with oxygen-free argon for the dark anaerobic fermentation. Pre-cultures of 1 L were used as inocula for 10 L Makkoli and Tofu wastewaters, respectively, in a 15 L stainless steel fermentor to produce Hydrogen and various organic acids. The immobilized *R. sphaeroides* E15-1, was evenly spread in the rectangular photo-fermentor (width x length x depth, 50 Cm x 50 Cm x 4 Cm). After the anaerobic fermentation of Makkoli wastewater, 3-5 L of broth was photo-fermented in the reactor under 154  $\mu$ M photon/m<sup>2</sup>/sec irradiance

using tungsten halogen lamps. For the scale-up experiments, the procedures were the same as above. The pre-treated sewage sludge was also used for the photo-fermentation under similar experimental conditions as above except the volume was reduced, because the sewage sludge was dark brown in color and the light transparency in the sewage sludge was lower than in other samples.

Horizontal and vertical type tubular flow reactors were employed for SCWG of organic wastes and microbial sludge to produce the hydrogen. The former was developed at Hawaii Natural Energy Institute and the latter was constructed at KIER after modifying the horizontal reactor system.

## 3. Results and Conclusion

### 3.1 Pre-treatment and Feeding

75 L of Makkolii and Tofu wastewaters was added without pre-treatment to a 100 L-capacity anaerobic fermentor (stirred-tank type) for hydrogen production. The fresh food processing wastewaters were exchanged three times a day from 9:00 am to 5:00 pm at the rate of 1.25 L/ min for 20 min of each exchange. The outflow from the anaerobic fermentor was collected to a settling tank for 3-5 hrs to separate the supernatant from the precipitate by gravity and the supernatant containing mainly organic acids was fed to the photo-bioreactor.

Fruit wastes were roughly cut and fed to the modified commercial juicer (screen diameter, 0.2mm) to separate the pulp from juice. The waste fruit juice containing 40-90 g reducing sugar / L was fed to the anaerobic

fermentor through a centrifugal pump without dilution.

### 3.2 Anaerobic fermentation.

*Cl. butyricum* NCIB 9576 produced approximately 1.1 L H<sub>2</sub> /L broth/day when the synthetic PYG media containing 1% glucose was used as a feed. The initial pH 6.8 decreased to 4.24.5 during the first 1216 h of fermentation when pH was not controlled, resulting in the arrest of the Hydrogen evolution and cell growth with only 80% degradation of added glucose. However, when pH was controlled to 5.5-6.0, glucose was

completely consumed, increasing Hydrogen production to 1.8 L H<sub>2</sub> /L broth/day. Organic acids and solvents were also produced during the anaerobic fermentation by *Cl. butyricum* NCIB 9576, which were mainly butyrate, acetate, propionate and ethanol. When pH of the broth was controlled to 5.56.0, acetate production was increased to a maximum of 16mM at 2024 h fermentation and then decreased to 10mM during 48h fermentation. Butyric acid did not accumulate until 20 h of fermentation but was slowly produced up to 30 mM during 48h fermentation. Approximately 12 mM and 2.5 mM of propionate and ethanol

Table 1. Composition of feeds to the biological hydrogen production reactors.

	Fruit wastes I	Fruit wastes II	F.P.W. I	F.P.W. II	S. Sl. I	S. Sl. II
Reducing Sugar (g/l)	93,466	48,395	0.940	0.736	0.08	0
Starch(g/l)	0	0	2.74	12.6	0	0
NH <sub>3</sub> -N (ppm)	ND	39.41	ND	5.66	37.2	45.0
TS (g/l)	86.5	64.64	16.7	17.3	10-23	6-13
SS (g/l)	2.7	7.80	12.4	1.4	2.2	7.2
VS (g/l)	41	51.64	14.94	12	1.84	3.4
BOD (mg/l)	71,100	58,400	20,580	9,060	3,120	ND
COD(mg/l)	53,216	47,094	13,330	22,000	2,040	ND

Fruit wastes I, winter fruit wastes containing mainly mandarin wastes from agriculture market.

Pretreated shown in the Experimental

Fruit wastes II, summer fruit wastes containing mainly watermelon wastes from agriculture market. Pretreated shown in the Experimental

F. P. W. I, food-processing wastewater from Makkoli (traditional rice wine) factory

F. P. W. II, food-processing wastewater from Tofu (soybean cake) factory

S. Sl. I, sewage sludge before heat treatment

S. Sl. II, sewage sludge after heat treatment

TS, total solid; SS, suspended solid; VS, volatile solid; NH<sub>3</sub>-N, ammonia nitrogen

ND, not determined

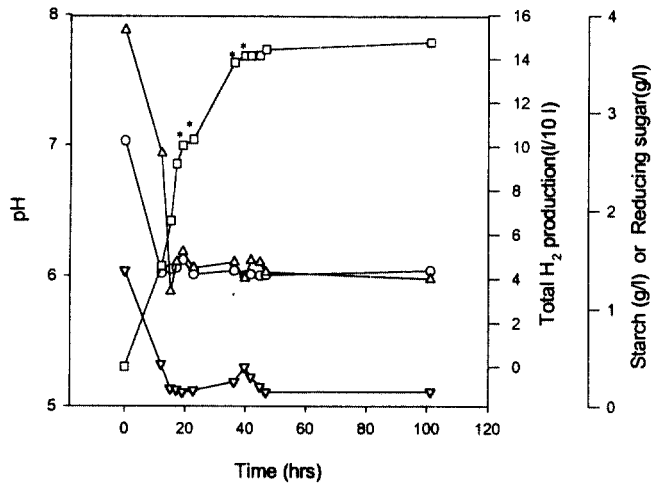


Fig. 2. Hydrogen production by anaerobic fermentation of Makkoli wastewater by *Cl. butyricum* NCIB 9576  
 -○-pH, -□- hydrogen, -△- starch, -▽- reducing sugar  
 -\*- 1.5L media exchange.

were produced during the anaerobic fermentation, respectively. The amounts of  $H_2$ , 1.1 L and 1.8 L, which were produced from 1 L synthetic PYG containing 1% glucose without and with pH control, are equivalent to about 0.89 and 1.46 mole of  $H_2$  /mole of glucose, respectively. As compared to the result of Heyndrickx et al<sup>8-9)</sup>, we produced about 8.7 times more Hydrogen but about 3.2 times less acetate under similar experimental condition but using different strains of *Cl. butyricum*. However, 1.46 mole of  $H_2$ / mole of glucose is still lower than the yield by Wood<sup>10)</sup>, which was 2.35 mole of  $H_2$ / mole of glucose in a test tube. These differences in the Hydrogen and organic acids production might be caused by the strain properties and the fermentation conditions.

Makkoli wastewater has a large variation in the contents of sugars, starch, and ethanol, which are in the range of 0.541.2 g/L, 2.53.8

g/L and 515 g/L, respectively. These variations were caused by the amount of water used for cleaning the fermentation tank, the period of sampling time and so on. In Korea, wastewater treatment utility is mandatory for Makkoli factory that has a capacity higher than 30,000 L/day Makkoli production. Unfortunately, more than 70% of Makkoli was produced by small scale local manufacturers and the wastewater is disposed to the drain, causing a serious contamination to sewage.

*Cl. butyricum* NCIB 9576 produced an average of 1 L  $H_2$  from 1 L Makkoli wastewater during the initial 18 h of the anaerobic fermentation by *Cl. butyricum* NCIB 9576<sup>11)</sup>. pH was initially adjusted to 7.0 and the low limit of pH was 6.0 at 37°C during the fermentation of 10 L wastewater in a 15 L fermentor(see Fig. 2). It is approximately equivalent to 1.70 mole of  $H_2$  /mole of glucose for Makkoli wastewater by assuming that the

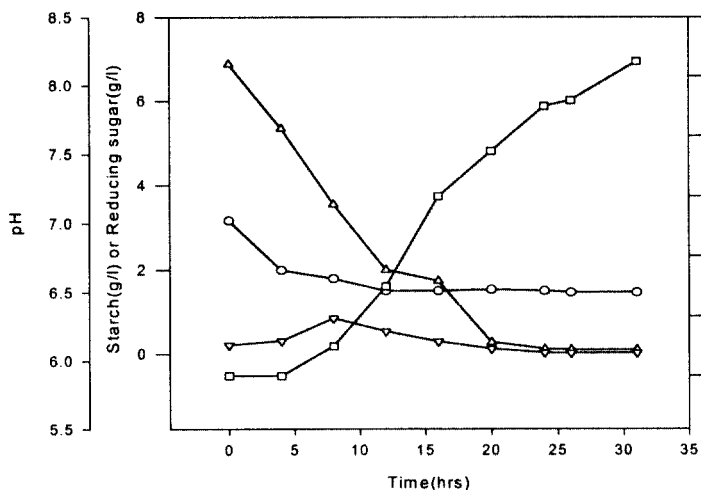


Fig. 3. Anaerobic fermentation pattern from Tofu wastewater by *Cl. butyricum* NCIB 9576 -○- pH, -□- hydrogen, -△- starch, -▽- reducing sugar.

conversion factor of soluble starch is 1.2. These results show that the Makkoli wastewater exhibits a better yield of H<sub>2</sub> production than the synthetic PYG media containing 1% glucose in which 1.46 mole of H<sub>2</sub> / mole of glucose was produced by *Cl. butyricum* NCIB 9576. When the cell concentration reached the maximum (dry cell wt., 1.2 g/L) and pH dropped to 6.0 after 20 h of batch fermentation, continuous fermentation of *Cl. butyricum* NCIB 9576 was performed. When the fresh Makkoli wastewater was added to the fermentor at the dilution rate of 0.15 h<sup>-1</sup> for 2 h, approximately 400 ml H<sub>2</sub>/L was additionally evolved for the next 15 h and then H<sub>2</sub> production ceased. The cell concentration dropped to 0.8 g/L with the supply of the fresh wastewater after 35-40 h of fermentation. The result indicates that the pH 6.0 of the fermentation broth is not sufficient for the growth of *C. butyricum* NCIB 9576.

Tofu wastewater, containing 5.0-8.0 g/L soluble starch and 0.3-0.4 g/L sugars, generated 0.9 l H<sub>2</sub>/L wastewater, along with some organic acid, during 26 h of fermentation. (see Fig. 3) Due to the higher concentration of soluble starch in Tofu wastewater compared to the Makkoli wastewater, it took an additional 6-8 h to reach the maximum Hydrogen production during the anaerobic fermentation. The rate of hydrolysis of soluble starch to produce sugars was faster than that of consumption of sugars by *Cl. butyricum* NCIB 9576 in Tofu wastewater, resulting in the slight increase of sugars after 8-10 h as shown in Figure 4. The Hydrogen production from Tofu wastewater using *Cl. butyricum* NCIB 9576 reached 1.05 l H<sub>2</sub> /L broth, which is equivalent to 0.97 mole of H<sub>2</sub> /mole of glucose, assuming that the conversion factor of soluble starch to sugar is 1.2. This result indicates that Tofu wastewater is less efficient for the Hydrogen production than Makkoli

which are used for the coagulation of soy protein curd, might cause the low efficiency of Hydrogen production by inhibiting the growth and other metabolism of *Cl. butyricum* NCIB 9576.

A stainless steel 100L-capacity stirred-tank type, anaerobic fermentor was manufactured from a local manufacturer. (see Fig. 4) The top part of the fermentor was connected to a feed tank through a centrifugal pump to feed the organic wastes and wastewaters. Outflow from the anaerobic fermentor was collected to a liquid-solid separator through a pump. The supernatant in the liquid-solid separator was fed to a photo-bioreactor whereas the cell debris and fruit residues, which precipitated at the bottom of the liquid-solid separator, were introduced to a supercritical water gasification reactor to produce hydrogen. The gases produced, of which about 40-60% was

Fig. 4. A 100 L-capacity stirred-tank type anaerobic fermentor.

wastewater which produced 1.70 mole of  $H_2$  /mole of glucose. The large amount of salts, such as  $Mg^{++}$  and  $Ca^{++}$  in Tofu wastewater

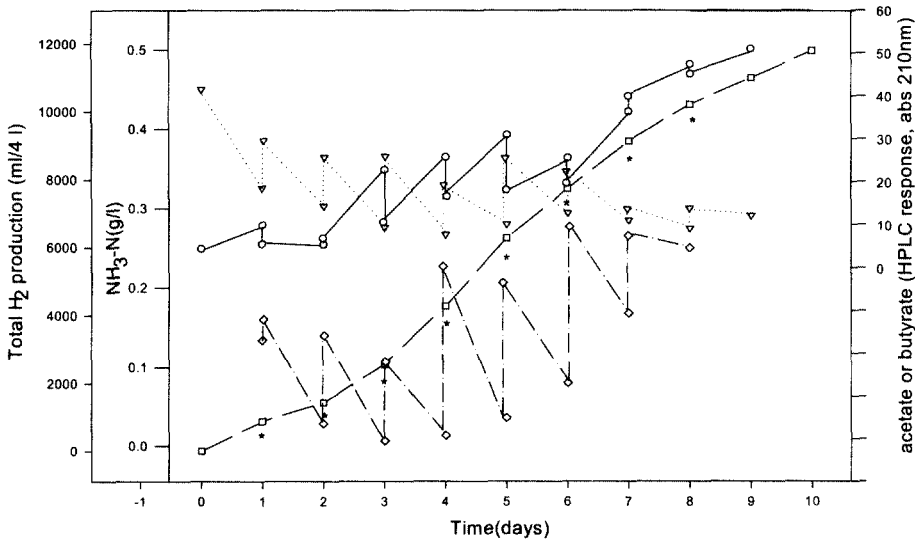


Fig. 5. Hydrogen production by photo-fermentation of the immobilized *R. sphaeroides* E15-1 from the remaining broth after anaerobic fermentation of Makkoli wastewater by *Cl. butyricum* -□- gas, -○- acetate, -△- butyrate, -◇-  $NH_3$ , -\*- 2L of broth exchanged.

hydrogen and the rest was CO<sub>2</sub>, were collected to a gas tank to 10 atm using an air-driven gas compressor, after moisture was removed. Microorganisms used in this research for the anaerobic fermentation were the sewage sludge from the digestion tank and/or the pure culture of *Cl. butyricum*. Hydrophilic cuprammonium rayon fibers were attached to the inside of the reactor to increase the population of microorganisms by immobilizing the cells and to prevent the bulking (floating) of culture in the reactor.

The maximum and average rate of hydrogen production were 118-178 ml/hr and 45-50 ml/hr, respectively from the synthetic media containing 1% glucose with the immobilized culture of *Cl. butyricum* at 37°C, pH 6.0-6.5 under anaerobic culture conditions. Under the same experimental conditions, the average of 53 L H<sub>2</sub>/day was evolved when 75 L of Makkoli

wastewater containing 0.7-1.0 g reducing sugars /L and 5-15 g ethyl alcohol /L was semi-continuously fed to the fermentor.

When combination of microbial sludges from a methane digester and the pure culture of *Cl. butyricum* were used as seed culture, 1.5 times more hydrogen was evolved than the pure culture only. The composition of the feed is shown at the Table 1 and the amounts of hydrogen produced were different depending on the composition of feeds used.

### 3.3 Photosynthetic cultivation

The broth remaining after the anaerobic fermentation of the PYG synthetic media containing 1% glucose, which had approximately 35 mM total organic acids, produced about 0.5 L H<sub>2</sub>/L-broth for 3 days of fermentation. The maximum rate of H<sub>2</sub> production was 0.38 L H<sub>2</sub>/L-broth/day and

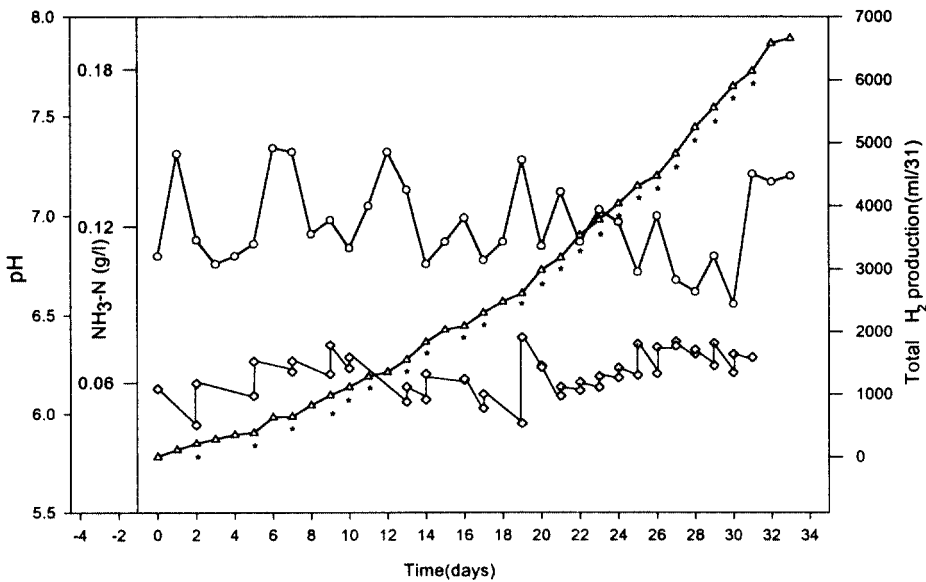


Fig. 6. Hydrogen production by the immobilized *R. sphaeroides* E15-1 using sewage sludge -○- pH, -△- Hydrogen, -◇- NH<sub>3</sub>-N.



Fig. 7. A 200 L flat type photo-bioreactor at outdoors.

80% of total organic acids were degraded during the first 24 h of photo-fermentation by *R. sphaeroides*. The broth remaining after the anaerobic fermentation of Makkoli wastewater, which comprised 30–40 mM organic acids, 0.1–0.2 g/L soluble starch, and 0.084–0.523 g/L  $\text{NH}_3\text{-N}$ , was used as a feed for the photo-fermentation by *R. sphaeroides* E15-1. The organic acids and solvent in the broth were mainly butyrate (29–37 mM), acetate (1–3 mM), ethanol (70–150 mM), and very little lactate and propionate.

After photo-fermentation for 1 day, fresh broth was added to the fermentor to replace the old broth at the dilution rate of 0.5 h<sup>-1</sup> for 1 h, every 24 h. About 0.44 L  $\text{H}_2$  was continuously evolved from 1 L broth for the 10 days of photo-fermentation (see Fig. 5). Butyrate, which was most abundant in the broth remaining after the anaerobic fermentation of Makkoli wastewater, was degraded 50–70% during the fermentation. Acetate was not metabolized by *R. sphaeroides* E15-1 and accumulated up to 16.9 mM for the

10 days of photo-fermentation. Accumulation of acetic acid during the photo-fermentation seems to be caused by two factors: the inability to metabolize acetic acid and the accumulation of acetic acid during the fermentation of sugars by *R. sphaeroides* E15-1. Ethanol in the broth was easily degraded 20–35% a day after the fresh media was supplied.  $\text{NH}_3\text{-N}$  contents of the broth remaining after anaerobic fermentation of Makkoli wastewater were in the range of 0.084–0.523 g/L.  $\text{NH}_3\text{-N}$  at a concentration below 0.3 g/L was metabolized about 80–96% by *R. sphaeroides* E15-1 in this experiment and did not affect Hydrogen production. However,  $\text{NH}_3\text{-N}$  was not degraded at a concentration above 0.3 g/L in the broth and the rates of butyrate and ethanol hydrolysis and Hydrogen production declined. In a preliminary experiment, Hydrogen production by *R. sphaeroides* E15-1 was inhibited by 0.5 g/L of  $\text{NH}_3\text{-N}$ . Sugars and starch were degraded well during hydrogen production and pH of broth dropped to 5.0–5.8.

Due to the high contents and variations of the soluble starch in Tofu wastewater, anaerobic fermentation by *Cl. butyricum* NCIB 9576 required longer fermentation time than Makkoli wastewater and the remaining broth showed a great deal of variation in carbohydrates composition. When 0.28 g/L soluble starch, 0.1 g/L sugars and 7.1-8.6 g/L total organic acids were present in the remaining broth from anaerobic fermentation of Tofu wastewater, Hydrogen production was approximately 0.40-0.45 L/L- broth/day and acetate was accumulated during photo-fermentation. However, when the composition of sugar, and total organic acids in the broth were standardized to that of anaerobic fermentation broth from Makkoli wastewater, about 0.2 l H<sub>2</sub>/L broth/day was continuously

produced for 10 days.

The sewage sludge used in this experiment was the returned sewage sludge which was collected from the aeration tank basin of municipal wastewater disposal utility. Sludge was composed of 98-99 %(w/w) total solid, 1.8 g/L volatile solid and less than 0.037 g/L NH<sub>3</sub>-N. Sugars and soluble starch contents were 0.07 and 0.001 g/L, respectively. Instead of anaerobic fermentation by *C. butyricum* NCIB 9576, sewage sludge was pre-treated with heat for 1 h at 150°C under 10 atm after alkali treatment to pH 14. In our preliminary experiment, the heat treatment without alkali treatment increased the NH<sub>3</sub>-N content and resulted in the decrease of hydrogen production by *R. sphaeroides*. The pH of the fresh sewage sludge was adjusted to pH 14 to

Table 2. SCWG of organic wastes at 700 °C, 27.6 MPa.

Feedstocks	M	D	PFM	AFD
Initial TCOD (mgO <sub>2</sub> /L)	37,403	17,419	11,333	26,280
Temperature (°C)	703	702	706	698
Gas production rate (L/h)	6.55	3.70	1.65	5.58
Gas composition (vol %)				
H <sub>2</sub>	49.12	38.79	54.80	49.37
CO	2.07	0.14	0.15	0.09
CO <sub>2</sub>	20.87	33.84	27.56	26.68
CH <sub>4</sub>	20.65	22.40	11.91	18.21
C <sub>2</sub> H <sub>4</sub>	0.24	0.62	1.53	0.58
C <sub>2</sub> H <sub>6</sub>	7.03	4.02	3.72	4.72
C <sub>3</sub> H <sub>6</sub>	0.00	0.11	0.28	0.16
C <sub>3</sub> H <sub>8</sub>	0.01	0.07	0.05	0.20
TCOD destruction (%)	99.58	95.70	93.20	95.20
PH	6.72	7.21	7.28	8.12

M, food-processing wastewater from Makkoli manufacturer

D, food-processing wastewater from Tofu manufacturer

PFM, Microbial sludge after biological hydrogen production of Makkoli wastewater

AFD, Microbial sludge after biological hydrogen production of Tofu wastewater

Fig. 8. A polymer electrolyte fuel cell and display panel.

strip the ammonia in the gas phase before heat-treatment. This procedure resulted in the decrease of  $\text{NH}_3\text{-N}$  content to 0.04-0.05 g/L. The pre-treated sewage sludge, which contained 25-40 mM organic acids, 0.04-0.05 g/L  $\text{NH}_3\text{-N}$  and a little amount of sugars, continuously produced 0.17-0.28 l  $\text{H}_2$ /L broth/day during the 30 days of photo-fermentation. The average of 154 M photon/ $\text{m}^2$ /sec irradiation was illuminated at the surface of the reactor using tungsten halogen lamps (see Fig. 6).

A 200 L-scale flat horizontal type photo-bioreactor was used at outdoors (see Fig. 7) for photobiological production of hydrogen using sunlight during the day and tungsten halogen lamps during the night. The reactor was located inside a green house built with vinyl film. The average illumination of the sunlight at the surface of reactor was 600-880 watts/ $\text{m}^2$  from 12:00-15:00 PM during summer. It sometimes caused the photo-inhibition resulting in the whitening of purple non-sulfur bacteria. The surface of the reactor was covered with a shade cloth during the

daytime of summer, and it reduced the illumination to 200 watts/ $\text{m}^2$  to avoid the over-exposure of sunlight. Approximately, 2,000-3,000 lux/ $\text{m}^2$  was illuminated during the night to maintain the culture activity.

The residue from the anaerobic fermentation of fruit wastes which contained mainly 50-150 mM lactate, and 250-670 mM butyrate was pumped into a 25 L reactor for 2 times a day during the day. The amount of hydrogen produced from the above was approximately 50-70 L per day.

The pre-treated sewage sludge by heat and pressure produced hydrogen 15.8 L per day during the initial 5 hrs of the photo-fermentation from the flat type photo-bioreactor. Tofu and Makkoli wastewaters were used for the production of hydrogen by anaerobic fermentation initially and then the outflow from the anaerobic fermentor was fed to the photo-bioreactor. The residues from anaerobic fermentation of Tofu wastewater produced average of 28.5 ml  $\text{H}_2$ /L/hr from the flat type photo-bioreactor and the total amount of hydrogen produced were 30-34 L per day using a 200 L flat type photo-bioreactor, while that of Makkolii wastewater, which contained more organic acids than Tofu wastewater fermentation residue produced average of 49.0 ml  $\text{H}_2$ /L/hr and total 45-50  $\text{H}_2$  per day at the same experimental conditions. The gas produced from the reactor was collected by the same method as in the anaerobic fermentor.

### 3.4 Supercritical water gasification (SCWG)

The horizontal tubular SCWG reactor, which

has a 0.622 x 0.953 x 116 cm (ID x OD x L) Hastelloy C-276 tube reactor, was operated at 28 MPa, 700°C with 21sec of HRT.

The outflow from the photo-bioreactor was fed to the SCWG reactor to produce hydrogen as well as to reduce COD of effluents. The hydrogen concentration was 39-55% of total gas produced under this experimental condition and 93-99% of the initial feed TCOD was removed. The reactor was often plugged with chars and tars when microbial sludges were operated longer than 10 hrs. To avoid the plugging in the reactor wall, a vertical type SCWG reactor was constructed to drain the chars and tars produced during the operation and to scale up the volume by 2 times. Approximately 10-15 L of microbial sludge per day was gasified by this reactor and an average of 150 L H<sub>2</sub>/day was produced and the operation period was extended up to 50 hrs. TCOD 11,000-26,000 mg O<sub>2</sub>/L of the microbial sludge was reduced to 700-1,100 mg O<sub>2</sub>/L. Biomass used in this study such as microbial sludge, sewage sludge, fruit wastes were good substrates for the hydrogen production by SCWG, the uniform feeding to the reactor was difficult due to the viscosity of the biomass itself.

### 3.5 Storage and separation of gas

The gases produced from the 100 L-anaerobic fermentor, 200 L-photobioreactor and SCWG reactor, were removed moisture and then stored to a 30 L-gas tank under 10 atm using an air-driven gas booster (Haskel Model AGT-4) at room temperature. The composition of total gas collected from the above three different reactors was mainly 35-58% H<sub>2</sub>, 5-30% CO, 19-31% CO<sub>2</sub>, 5-11%

CH<sub>4</sub> and the small amounts of ethane, ethylene and propylene. The pressure swing adsorption method was used to separate hydrogen from other gases. The adsorption materials, zeolite, active carbon and alumina were charged to 3 different towers to adsorb the gases except hydrogen. The final hydrogen concentration was 98.45-99.53% and it was re-stored to 30 L-capacity gas cylinders under the pressure to 10 atm.

### 3.6 Electrical power generation by a fuel cell

A polymer electrolyte fuel cell was composed of 24 stacked single cells and each single cell had 50 cm<sup>2</sup> of electrode surface area. It was connected to hydrogen and air tanks to generate 60 watts (12 volts, 5 amps) electric power.

A 30 L-capacity hydrogen gas cylinder under the pressure of 10 atm, which has total 300 L hydrogen, was used to generate electricity to turn on the halogen lamps (60 watts) in the display panel board for 5 hrs (see Fig. 8).

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