# Hydrogen Production by Photosynthetic Microorganisms

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# **ABSTRACT**

Hydrogen is a clean energy alternative to the fossil fuels, the main source of greenhouse gas emissions. We developed a stable system for the conversion of solar energy into hydrogen using photosynthetic microorganisms. Our system consists of the following three stages:

- 1. Photosynthetic starch accumulation in green microalgae (400 L ×2);
- 2. Dark anaerobic fermentation of the algal starch biomass to produce hydrogen and organic compounds (155 L ×2); and
- 3. Further conversion of the organic compounds to produce hydrogen using photosynthetic bacteria (three types of reactors, parallel plate, raceway, and tubular).

We constructed a test plant of this process at Nankoh power plant of Kansai Electric Power Company in Osaka, Japan, and carried out a series of tests using CO<sub>2</sub> obtained from a chemical absorption pilot-plant. The photobiological hydrogen production process used a combination of a marine alga, *Chlamydomonas* sp. MGA 161 and marine photosynthetic bacterium, *Rhodopseudomonas* sp. W-1S. The dark anaerobic fermentation of algal starch biomass was also investigated. Sustained and stable starch accumulation, starch degradation in the algal cell, and hydrogen production from algal fermentation and photosynthetic bacteria in the light were demonstrated during several experiments.

**Index Entries:** Microalgae cultivation; algal fermentation; photosynthetic bacteria reaction; raceway reactor; parallel plate reactor.

# INTRODUCTION

The sustainable development of human activities in harmony with the global environment can be achieved by increasing the recycling of the resources neces-

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sary for those activities. Hydrogen is a clean, renewable form of energy, convenient to store and transport. It can be converted to electric energy with high efficiency. Hydrogen production by biophotolysis of water based on microalgal photosynthesis in the carbon recycling system is an ideal solar energy-conversion system for sustainable human activities in harmony with the global environment.

Based on the studies that have been conducted on a small-scale (1-3), we constructed the bench-scale test apparatus at the Nankoh power plant of Kansai Electric Power Company in Osaka, Japan. In this article, a series of the test results using this apparatus are reported.

# SYSTEM OF PHOTOBIOLOGICAL HYDROGEN PRODUCTION

The photobiological hydrogen production system that has been studied is shown in Fig. 1. This system consists of the following four processes:

- 1. Cultivation of microalgae: In this process, starch is made from microalgal photosynthesis. The microalgae marine *Chlamydomonas* sp. MGA 161 was used.
- 2. Fermentation of microalgae: In this process, organic products, such as acetic acid, ethanol, and glycerol, are produced from the dark anaerobic reaction of the starch in the microalgae that was produced in the prior process.
- 3. Separation of microalgae: After the fermentation was completed, the microalgal suspension liquid was treated by the microfilter. Concentrated microalgae was recycled to the alage cultivation pond, and permeate containing organic compounds was transferred to the H<sub>2</sub> production process.
- 4. Hydrogen production by photosynthetic bacteria: Organic products, such as acetic acid, ethanol, and glycerol, produced in the prior process were converted to hydrogen using photosynthetic bacteria in the light. The photosynthetic bacteria marine *Rhodopseudomonas* sp. W-1S was used.

In this hydrogen production system, it is necessary to recycle the microalgae to the algae cultivation pond after fermentation.

# **CULTIVATION OF MICROALGAE**

# **Test Apparatus**

In Fig. 2, the picture of the raceway-type reactor used in the cultivation of *Chlamydomonas* MGA 161 is shown. The specifications of this reactor are as follows:

Material acrylic resin

Size  $2800 \times 800 \times 250$  (depth) mm

Area 2 m²
Capacity 400 L
Agitator paddle type

# **Test Results**

In Fig. 3, algal productivity of *Chlamydomonas* MGA 161 in a raceway-type cultivator, using  $CO_2$  obtained from a chemical absorption pilot-plant treating actual power plant flue gas, is shown. The average productivity of the microalgae was  $15 \, \text{g/(m^2 \cdot d)}$ , and the maximum starch content of microalgae was about  $40 \, \text{wt}\%$ .

In Fig. 4, the relationship between the productivity and content of starch is shown. The productivity of starch becomes maximum in the range of starch content

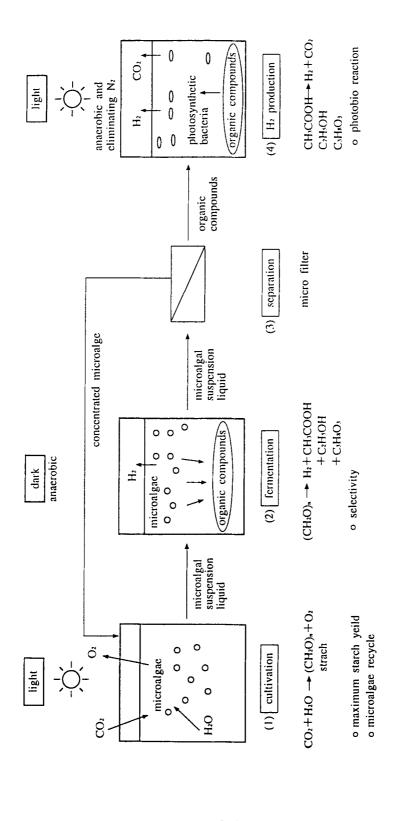


Fig. 1. Process of photobiological hydrogen production by a combination of Chlamydomonas sp. MGA 161 and Rhodopseudomonas sp. W-1S.

2H<sub>2</sub>O→O<sub>2</sub>+2H<sub>2</sub>

orverall reaction

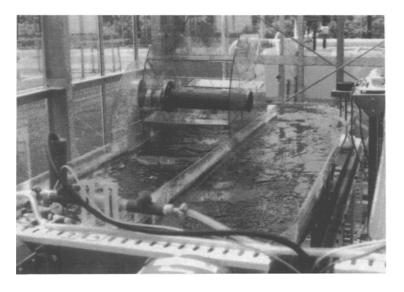


Fig. 2. Raceway-type cultivator.

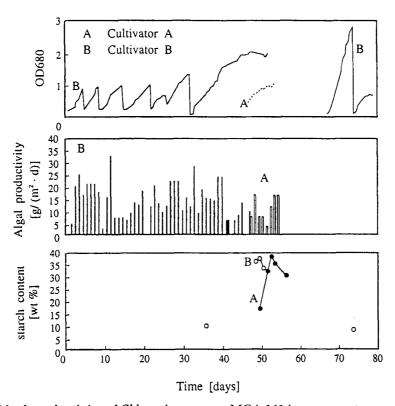


Fig. 3. Algal productivity of Chlamydomonas sp. MGA 161 in raceway-type cultivator.

from 20–30 wt% (dry). Therefore, microalgae (same microalgae are used repeatedly between cultivation and fermentation processes) should be subjected to the fermentative part of this process when the starch content reaches this range.

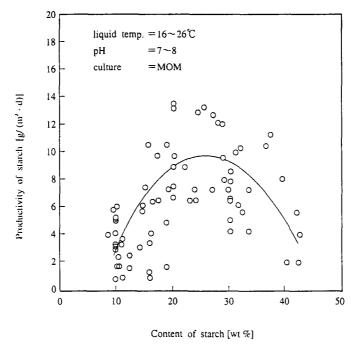


Fig. 4. Relationship between productivity and content of starch in the cultivation of *Chlamydomonas* sp. MGA 161.

# FERMENTATION OF MICROALGAE

# **Test Apparatus**

In Figs. 5 and 6, a photograph and the construction plan of the fermentor used in the test are shown. The specifications of this fermentor are as follows:

Material polyvinyl chloride

Size 450 mm in diameter × 1250 mm

Capacity 155 L

### **Test Results**

In Table 1, the results obtained with a small-scale test system that was conducted separately as a preliminary test are shown. The influence of the gas-phase Composition of the fermentor on the productivity of organic compounds in the fermentor and hydrogen productivity in the photosynthetic bacterial reaction are shown. When  $CO_2$  was used in the gas phase of the fermentor, hydrogen production from the fermentor and the photosynthetic bacterial reactor was maximum. Organic compound productivity was the highest in this case.

The relationship between productivity of organic products and starch decomposition amount in the microalgae x is shown in Fig. 7. This relationship should be y = 2x, theoretically, but in this test, the relationship y = 1.6x was obtained. The reason for this is that another product, such as lactic acid, may be produced in addition to acetic acid, ethanol, and glycerol.

In Fig. 8, the relationship between productivity of organic products and concentration of microalgae is shown. This relationship is shown as a straight line up

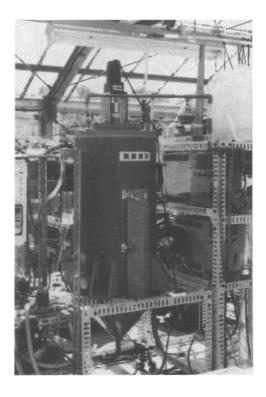


Fig. 5. Fermentor of microalgae.

to the microalgae concentration  $5000\,\mathrm{mg/L}$ , suggesting that in order to increase the organic compound concentration during fermentation, the microalgal suspension liquid should be concentrated.

# HYDROGEN PRODUCTION BY PHOTOSYNTHETIC BACTERIA Test Apparatus

Figure 9 pictures various types of reactors using *Rhodopseudomonas* W-1S as the photosynthetic bacteria. The specifications of these reactors are as follows.

priorosyritrictic bacteria. The s	peemeations of these reactors are as for
Parallel-plate-type	
Plate size	$990 \times 32 \times 490$ (height) mm
Number of plate	3
Spacing of plates	91 mm
Raceway type	
Size	$1100 \times 500 \times 12$ (depth) mm
Tubular-type	
Tube size	$30 (id) \times 1000 mm$
Number of tubes	10
Common item of reactors	
Material	Acrylic resin
Optical area	$0.5 \text{ m}^2$
Culture volume	60 L
	Parallel-plate-type Plate size Number of plate Spacing of plates Raceway type Size Tubular-type Tube size Number of tubes Common item of reactors Material Optical area

 $0.1 \, \text{m/s}$ 

Liquid velocity

(including reservoir volume)

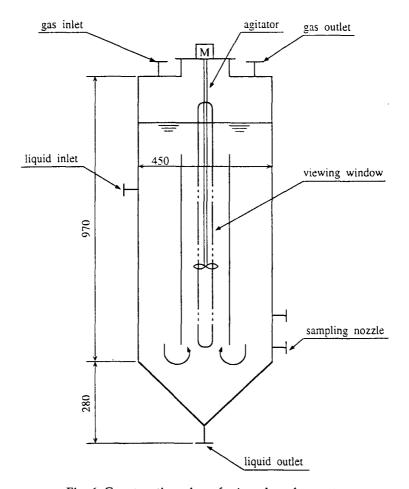


Fig. 6. Construction plan of microalgae fermentor.

# **Test Results**

In Fig. 10, the hydrogen productivity Q (NL/d)' of the three types of photosynthetic bacterial reactors, using fermentative products is shown. The Q of the parallel-plate-type reactor is the largest and second is the raceway-type reactor. The Q of the tubular-type reactor is one-sixth that of the parallel-plate-type reactor.

The reason why the Q of the parallel plate is the highest is that the optical efficiency is highest among the three reactors. The reason why the Q of the tubular reactor is the lowest is that the liquid volume, which is actually lighted, is 13 L and almost all the liquid stays in the reservoir. From the above test results, the parallel-plate-type reactor was selected.

Figure 11 pictures the large parallel plate reactor, which was used in a combined test with a microalgae cultivator and a microalgae fermentor. The specifications of this reactor are as follows:

Material Acrylic resin

Plate size  $2000 \times 50 \times 500$  (height) mm

Number of plates 6 Spacing of plates 120 mm

Table 1

	] on the Productiv	Influence of the Gas-Phase Composition of the Fermentor ivity of Organic Compounds in the Fermentor and Hydrog	s-Phase Compositi	on of the Ferr mentor and F	Influence of the Gas-Phase Composition of the Fermentor on the Productivity of Organic Compounds in the Fermentor and Hydrogen Productivity	
		in Photo	in l'hotosynthetic Bacteria Keaction	Keaction		
					Photosynthetic bacteria reaction <sup>b</sup>	Total H
		Ferme	Fermentation <sup>a</sup>		mmol/mg	productivity,
Gas composition	Acetic acid	Ethanol	Glycerol	$H_2$	$H_2$	gm/lom <sub>d</sub>
100% N,	66.0	0.46	0.08	1.68	2.24	3.92
100% CÔ,	0.57	0.39	0.40	0.40	5.89	6.29
100% H <sub>2</sub> <sup>1</sup>	0.19	0.44	0.82	Z.Ö.	0.15	N.D.
90% N <sub>2</sub> 10% H <sub>2</sub>	0.15	0.78	29.0	-2.66	1.34	-1.32
$80\% N_2  20\% H_2  50\% N_2$	0.14	1.29	0.57	-2.68	0.13	-2.55
50% N <sub>2</sub> 50% H <sub>2</sub> 50% C <sub>2</sub>	0.11	0.51	0.61	N.D.	0.12	N.D.
$10\mathrm{H_2}$	0.38	0.53	1.00	-1.81	4.68	2.87
50% CO <sub>2</sub> 50% H <sub>2</sub>	0.20	0.51	1.08	N.D.	4.29	N.D.

<sup>a</sup>Fermentation = 12 h.

<sup>b</sup>Photosynthetic bacteria reaction = 24 h.

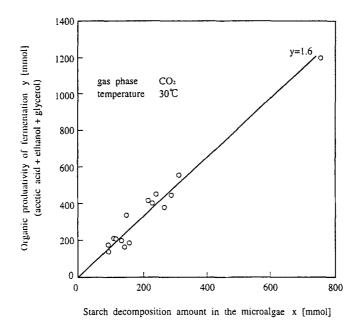


Fig. 7. Relationship between organic productivity and starch decomposition amount in the fermentor.

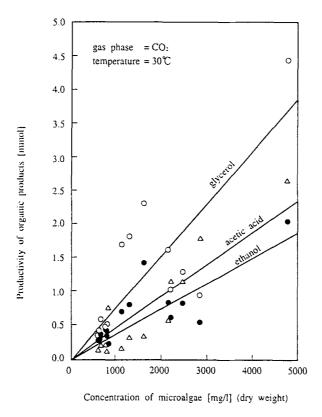


Fig. 8. Relationship between productivity of organic products and concentration of microalgae.

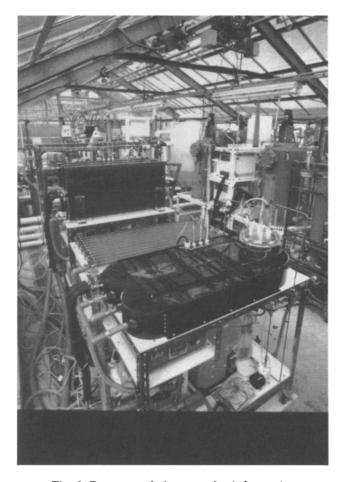


Fig. 9. Reactors of photosynthetic bacteria.

Optical area 1.8 m<sup>2</sup>
Culture volume 150 L

Testing of this reactor is now under way.

#### MICROALGAE RECYCLING TEST

In this hydrogen production system, it is necessary to recycle the microalgae to the algae cultivation pond after fermentation is completed.

In Fig. 12, the result of the microalgae recycling test is shown. The photosynthetic starch accumulation and fermentative production of organic compounds through starch degradation were carried out during an alternating light–dark cycle. Stable starch accumulation was repeatedly observed in the light period of this cycle. The fermentative production of acetic acid, ethanol, and glycerol occurred stably during the dark period of this cycle.

# **CONCLUSIONS**

1. The productivity of starch is maximum in the range of starch content from 20–30 wt%. Therefore, microalgae (same microalgae are used repeatedly

bacteria		Rhodopseudomonas Sp. W-1S		
reactor types		raceway	tubular	parallel plate
liquid volume		45	13	60
area [m²]		0.5		
Carbon source (actual products of fermentation)	acetic acid [mM]	0.53		
	ethanol [mM]	0.78		
	glycerol [mM]	2.0		

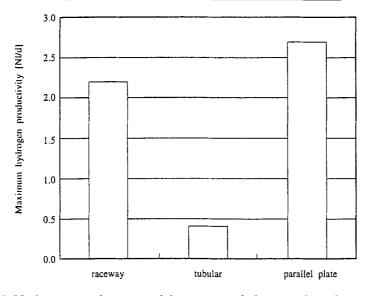


Fig. 10. Hydrogen productivity of three types of photosynthetic bacterial reactors.

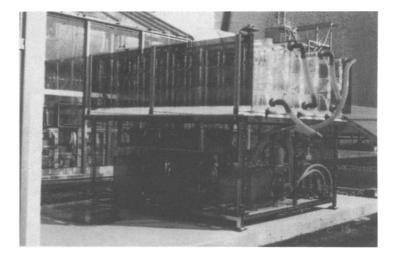


Fig. 11. Large-scale photosynthetic bacteria reactor.

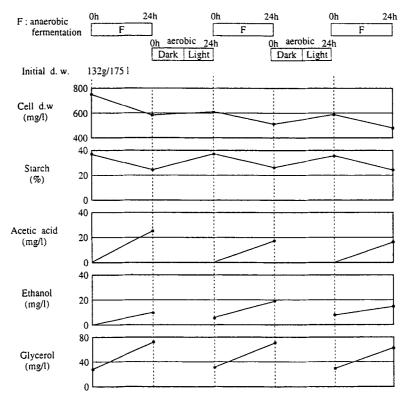


Fig. 12. Photosynthetic starch accumulation in a 400-L cultivator and the fermentative production of organic compounds in a 155-L fermentor by *Chlamydomonas* sp. MGA 161 in an alternative light–dark cycle.

between cultivation and fermentation process) should be subjected to the fermentative part of this process when the starch content reaches this range.

- 2. A microalgae recycling test was conducted. Photosynthetic starch accumulation and fermentative production of organic compounds through starch degradation occurred during an alternating light-dark cycle without any damage to the microalgae.
- 3. Three types of photosynthetic bacteria reactors were tested for hydrogen generation, and it was found that the hydrogen productivity of the parallel-plate-type reactor was the greatest.

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