H_2 PRODUCTION by DARK FERMENTATION from FOOD WASTES

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Objectives

Long term continuous H_2 fermentation
without sterilization (mixed culture)

Repress lactate and/or methane production by controlled fermentation

Decompose and dissolve solid wastes quickly and efficiently → suitable as a pre-treatment process of methane fermentation

Comparison of gas contents between hydrogen fermentation and methane fermentation

Hydrogen fermentation		Methane fermentation	
H_2	: 50-60%	CH_4	: 65-75%
CO_2	: 40-45 %	CO_2	: 25- 35 %
N_2	: 0-5 %		
H_2S	: ~ND	H_2S	: ~5000 ppm

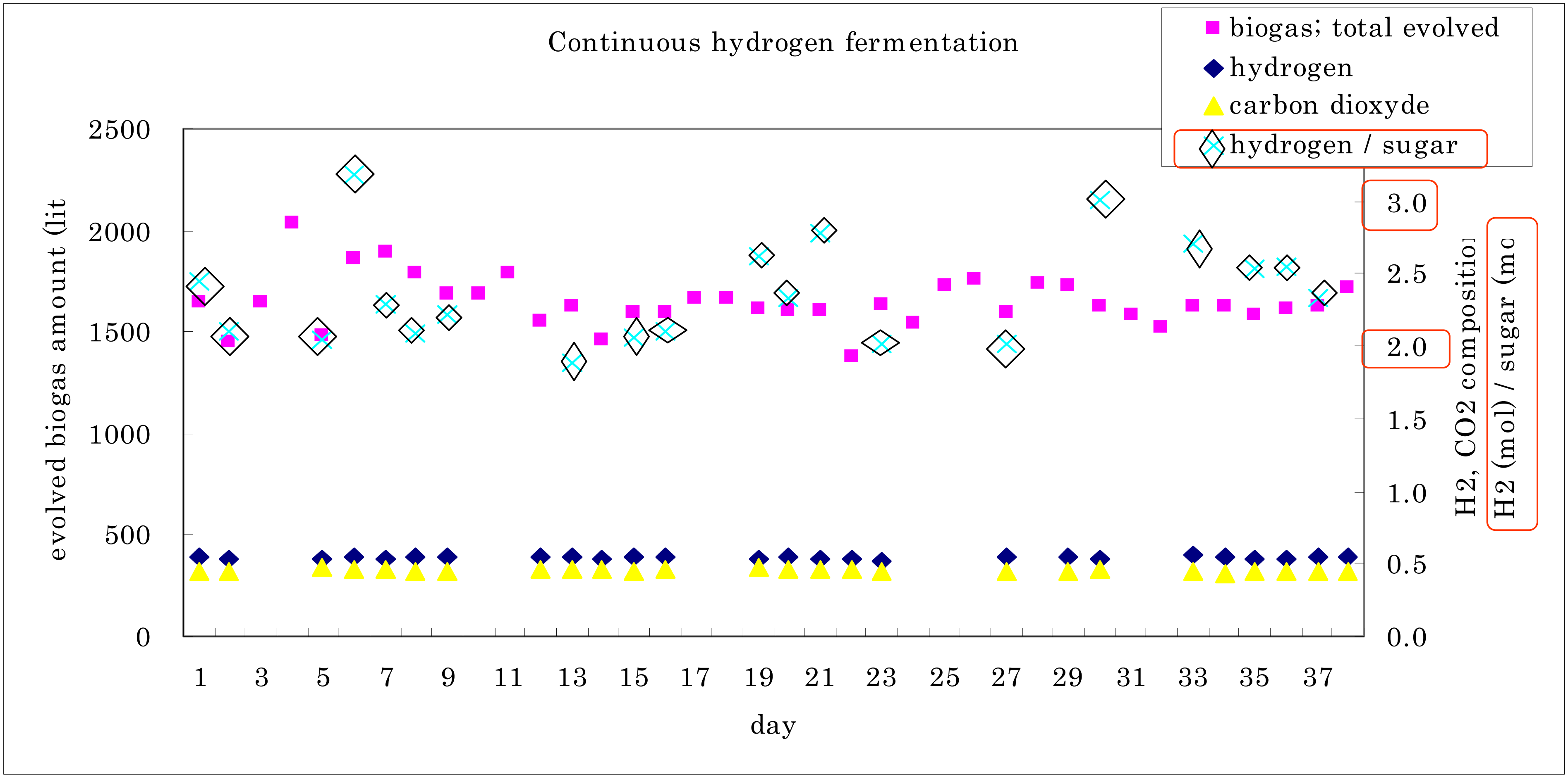
1 L-scale bench reactor

30 L lab. scale reactor

900 L pilot reactor (left tank)

inside of mixing tank (right)

Dark fermentation of hydrogen from bread in 900 litter-scale pilot reactor



Summary

- **Continuous fermentation (without sterilization): <u>6 months to 1year</u>**

  (lactate and/or methane production were successfully repressed)

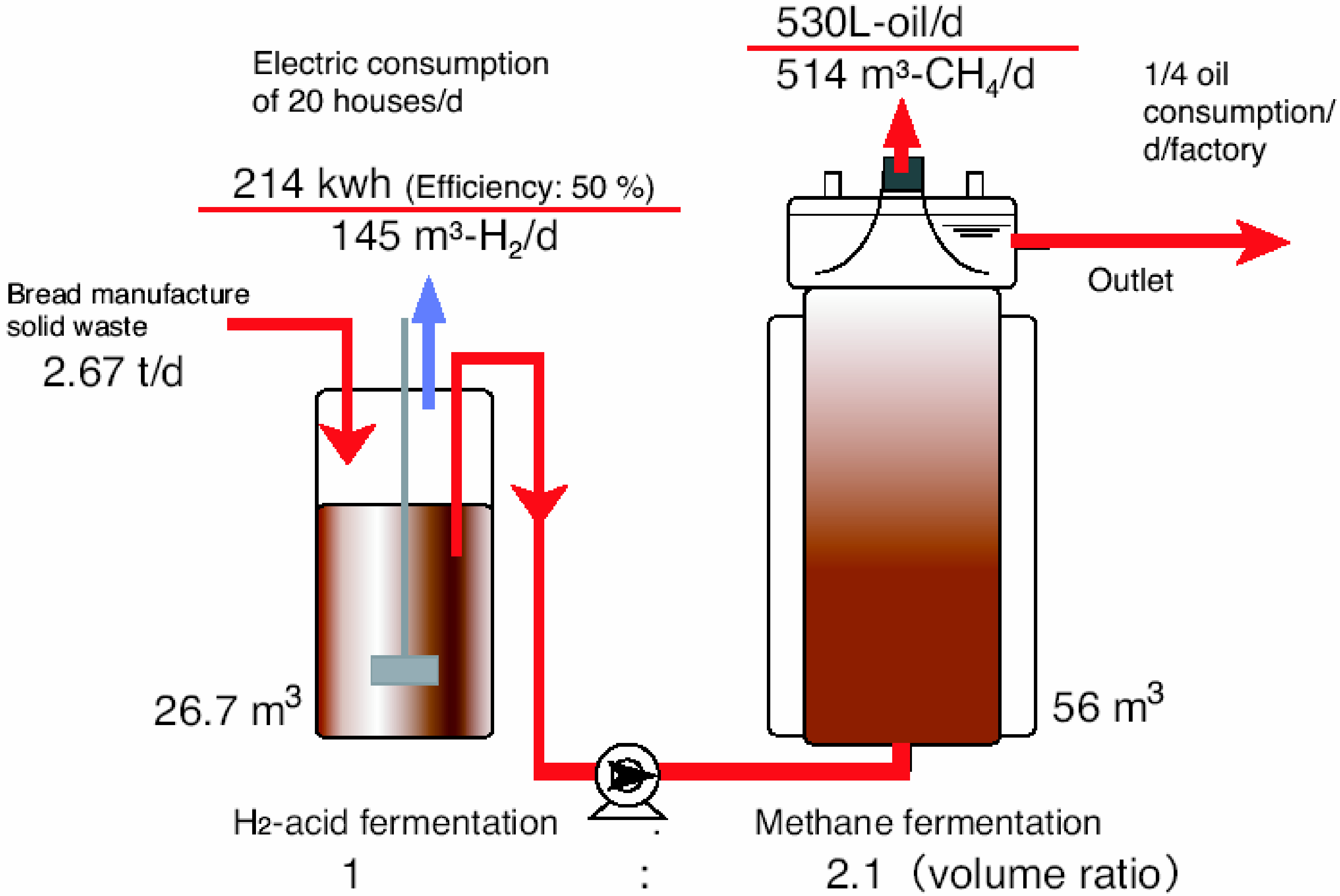
- **Hydrogen yield ratio： <u>2 to 3 moles／mole-glucose</u>**

- **Over 80 % of bread waste was decomposed and dissolved within <u>1-2days</u>,**

  (only a quarter of the conventional processing time)

- **H2 production: ～1000L/day /500L liquid / (6kg of solid bread in 250L/day)**

- **pH：6.0-6.5, temp. :50-60℃**
- **Dilution late： 0.5 / day**
- **H_2S content： less than 0.2ppm**



Estimation of energy recovery from bread solid wastes

Total Energy Balance Comparison between the Hydrogen - Methane Two-stage Fermentation and the Methane single Fermentation in the case of Brewery Effluent

		Generated gas amount	Energy balance		Mass balance
Pressed filtrate of spent malt #200 sieved					COD ~30,000 mg/L
Two-stage fermentation	Hydrogen fermentation (former stage)	1.76 L-H_2 / L-supplied liquid	23 kJ / L-liquid	283 kJ / L-liquid	COD removal ~10%
	Methane fermentation (latter stage)	6.54 L-CH_4 / L-supplied liquid	260 kJ/ L-liquid		COD removal ~65%
Methane single fermentation		6.67 L-CH_4 / L-supplied liquid	265 kJ/ L-liquid	265 kJ / L-liquid	COD removal ~85%

Reference : MITANI, Y. et al. MBAA (Master Brewers Association of the Americas) TQ vol.42 pp.283-289 (2005)

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Introduction

Methane fermentation by the Upflow Anaerobic Sludge Blanket (UASB) system is extensively applied to treatment of brewery effluents. However, the UASB system is not suited to process solid sludge. Therefore, the feed solution requires a pretreatment to remove any suspended solid matter. For example, the pressed filtrate from the spent malt of the lauter tun contains suspended matter at high concentrations (~60,000 ppm in COD). Physical removal of the suspended matter from this filtrate lowers the concentration (10,000 - 30,000 ppm). If it is possible to convert the suspended matter into biogas, more than twice the volume of biogas would be obtained.

Some bacteria found from the anaerobic fermentation decompose high-molecular polysaccharides to low molecular sugars and organic acids, generating hydrogen as a metabolite. We present an empirical study of dark fermentation of Hydrogen directly from bread waste containing high solid matter.

This approach is also expected to apply as Hydrogen-Methane Two-Stage Production

Corrosive sulfur has been a major problem in attempting to use biogas in fuel cells. Our experimental system can generate sulfur-free bio-hydrogen for over 6 months by controlling the fermentation processes. This system successfully decomposed and dissolved over 80 percent of bread waste within only a quarter of the conventional processing time.

This technology expected to apply wide-range of organic wastes.

Materials and methods

1. Hydrogen fermentation effective microorganisms

Hydrogen fermentation effective microorganisms were accumulated as follows; The anaerobic sludge (Hiroshima sewage treatment plant) were acclimatized for about one month in the bread processing effluent. The anaerobic sludge and the pressed filtrate are placed in a glass bottle. The microorganisms were cultured for 24 hours. The generated gas was collected in collection bags. Every 24 hour of cultivation a part of culture medium was removed and replaced by the fresh medium. The pH value of medium was adjusted to 7.0 before use.

2. Batch and continuous fermentation

The acclimatized hydrogen fermentation culture broth and the mixed bread waste were fed to the fermentor. The microorganisms were cultured batchwise for 3 days, then the fermentation was switched to a continuous mode (chemostat) at 50-60ºC.

3. pH value on hydrogen fermentation

Hydrogen fermentation was done at a pH range of from 6.0 to 6.5, according to our previous work; Mitani, Y. et al. "Hydrogen and Methane Two-Stage Production Directly from Brewery Effluent by Anaerobic fermentation" MBAA TQ vol. 42, no. 4, pp. 283-289 (2005)

4. Analysis

Generated gases

The generated gases were collected in collection bags. The gases produced from the fermentations were analyzed by the TCD-detector-equipped gas chromatograph (GC-8A Shimadzu Corporation).

Organic acids

Organic acids were determined using HPLC system (organic acid analyzing system, Shimadzu Corporation).

Sugars

Reducing sugars were analyzed by the HPLC system (reducing sugar analyzing system, Shimadzu Corporation). Total sugar content was determined by means of the phenol sulfuric acid method.

Effluent property

COD and BOD value was determined by the JIS K 0102 (1998) 20 and the JIS K 0102 (1998) 21 and 32.3. respectively. Suspended Solid matter was determined in the following manner; ten ml of the sample was taken and was filtrated by a glass filter (G100, Toyo Roshi, Tokyo), then the filter was dried and was weighed.

Conventional Treatment of Solid Waste from Bread Manufacture

T comp. H factory 16t/week

45% → Farmers

55% → Companies

Farmers → Animal feed

Companies → Animal feed

Animal feed → Decrease of Demand

Development of Treatment Process – Energy Recovery under low cost

Bread wastes → High rate H_2-CH_4 Two-Stage Process

Methane fermentation of H_2 fermented culture broth in UASB reactor

First stage:
liquefaction and H_2 fermentation

100 (g-wet/L) → 24(h)

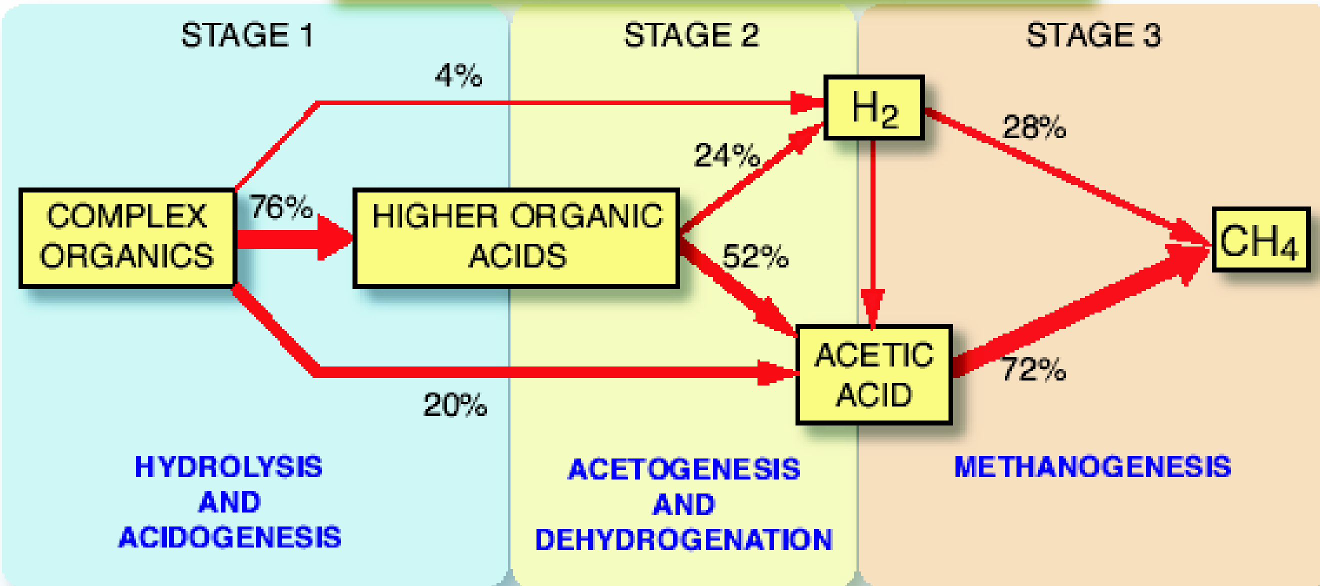
Solid reduction	91(%)
H_2 yield	2.43 (mmol/g-w. mat.)
Soluble TOC	20000 (ppm)

↓

Second stage:
UASB methane fermentation

Stages of methane fermentation

McCarty, P.L., (1982)



Traditional Methane Fermentation (Single-Stage Met Process)

Organics → CH_4

Two-stage Methane Fermentation (Two-Stage Met Process)

Organics → H_2 + VFA → CH_4

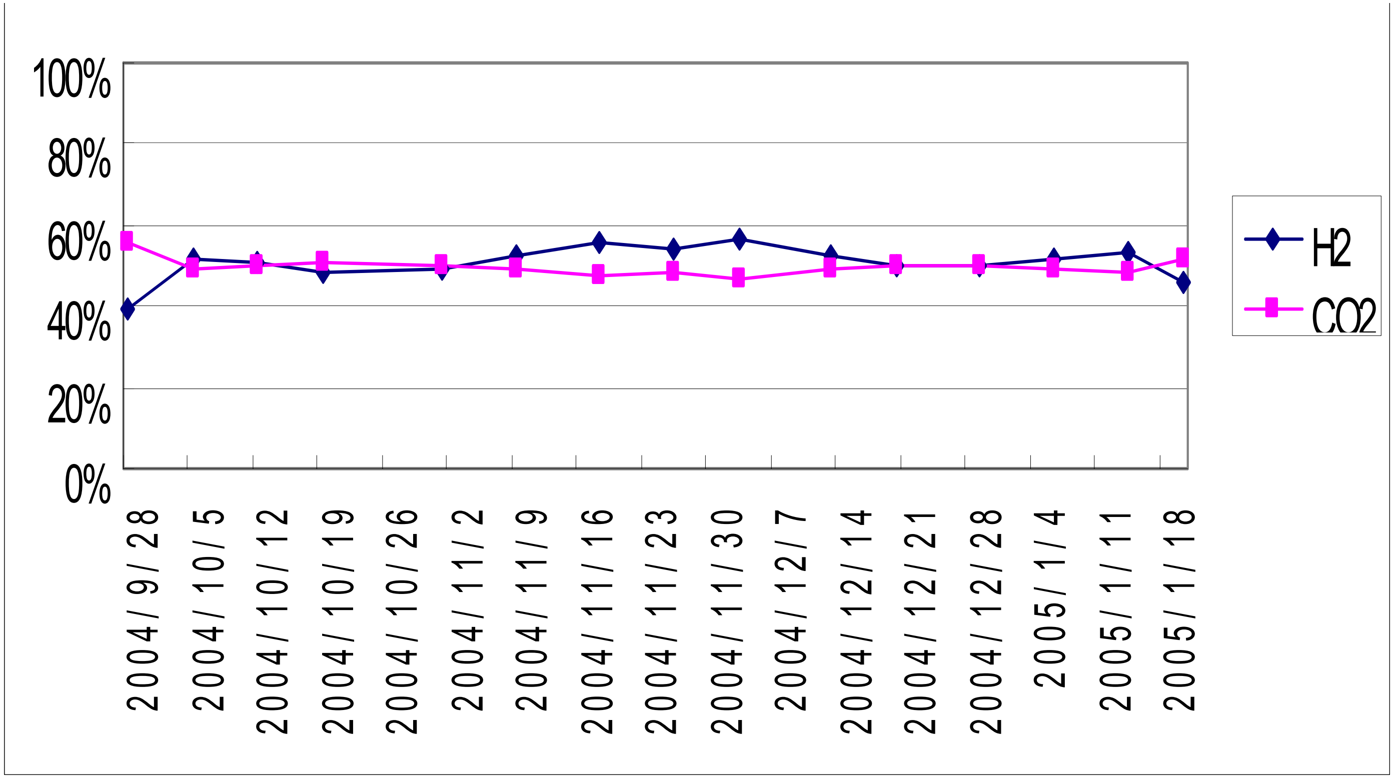
Two-stage Hydrogen-Methane Fermentation (Hy-Met Process)

Organics → H_2 + VFA; H_2 → H_2; VFA → CH_4

Summary

	Stage		Total
	1st	2nd	
Waste loading rate (g-wet/l/d)	100	—	32.3
Solid reduction (%)	91	—	91
Solid reduction rate (g-w. w./l/d)	91	—	29.4
H_2 yield (mmol-H_2/g-w.w.)	2.4	—	2.4
CH_4 yield (mmol-CH_4/g-w.w.)	—	8.6	8.6

Gas content of continuous fermentation in 30L scale reactor using bread waste



PREFACE

A bio-hydrogen project has started in 2002FY, sponsored by Ministry of Agriculture Forestry and Fisheries, Japan, a part of National Millennium Foundation, named "Biomass Nippon".

Microbial hydrogen production coupled with bio-degradation of organic substrates is an attractive approach to reducing organic wastes as well as generating energy.

Thus this project aims to develop basic technologies using microbial function to degrade food waste and recover as hydrogen energy.

To achieve these new technologies the project consists of the following research areas;

- **Metabolic engineering for dark fermentation in Enteric bacteria;**
- **Cascade reactor with hydrogen-methane two-step fermentation;**
- **H_2 production by co-cultivation with acid-producing bacteria and anoxygenic phototrophs;**
- **Small size bioreactor (Micro-Bioreactor) for portable bio-fuel cell systems;**
- **Protein designing for the "Bio"(enzymatic)- fuel cell by direct energy conversion from sugar to electricity;**

In this conference, we present selected topic from above research areas, especially in "<u>macro</u>" scale hydrogen bio-reactors for bread wastes.

R&D for Microbial/Biochemical Energy Conversion and Hydrogen Fermentation Technologies

A National Bio-Hydrogen Project in Japan

financially supported by Ministry of Agriculture, Forestry and Fisheries

- a part of *BIOMASS-NIPPON* Principle -

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Metabolic engineering for dark fermentation in Enteric bacteria;

Cascade reactor with hydrogen-methane two-step fermentation;
-Dark fermentation with bread solid wastes

H_2 production by co-cultivation with acid-producing bacteria and anoxygenic phototrophs;

Small size bioreactor (Micro-Bioreactor) for portable bio-fuel cell systems;

Protein designing for the "Bio"(enzymatic)- fuel cell by direct energy conversion from sugar to electricity;

Dark fermentation with bread solid wastes

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Hiroshima University and Sapporo Breweries Ltd.

Summary

- **Continuous fermentation (without steril and over 6 months days in 900L**
- **Hydrogen yield ratio： 2 moles／mole glucose**
- **Dilution late： 0.5 ／day**
- **H_2S content： less than 0.2ppm**

1 and 30Litter bench scale reactors

1 litter scale reactor

30 litter scale reactor

900litter-scale pilot reactor