Fermentative Hydrogen Production with a Small Pilot Plant by using Molasses as Substrate

Shigeharu Tanisho*, Hiromichi Miyahira, Toshihiro Hayashi and Yukinori Hasegawa

BioHydrogen Technologies, Inc., 1-1-7-207 Tsutsumi,Chigasaki 253-0006, Japan
**E-mail: tanisho-shigeharu-fx@ynu.ac.jp*

Abstract

Hydrogen was produced from molasses by a small pilot plant equipped with 200L volume of fermenter. The fermenter contained 160L fermentation liquid and 80L was exchanged periodically with new feed. A newly found microflora was used as the organisms of the hydrogen fermentation. The hydrogen productivity of the microflora was examined under three kinds of hydraulic retention time (HRT) of the feed such as 6, 12 and 24hours. Biogas production rate and the yield of biogas were ca. 100L/h and ca. 3.0mol-biogas/mol-hexose at 6hr-HRT, ca. 75L/h and ca. 4.6mol-biogas/mol-hexose at 12hr-HRT, and 60L/h and ca. 6.6 mol-biogas/mol-hexose at 24hr-HRT. The only thing was that the biogas consisted of H_2 and CO_2 contained hydrogen only ca. 30% while 52% at 3L bench scale fermenter experiment. However, since the hydrogen yield at 24hr-HRT becomes ca. 2.0mol-H_2/mol-hexose, the flora is a hopeful microflora for hydrogen production.

1. Introduction

These days, many international committees on TPP are held to get agreement between the nations concerned. The treaty will be of crucial significance to Japanese agriculture, especially to Okinawa prefecture, because the prefecture doesn't have central industries and economical foundations to overcome newly arising problems. Figure 1 shows the transition of the total and top 4 amounts of agricultural products in Okinawa. From the graph, you can realize that sugar cane has been the leading product for long years. Even in 2012, the cultivated acreage of sugar cane occupied ca. 50% as 18,600ha in 39,000ha of total farming land. So far Japanese government has guaranteed sugar cane farmers of their steady income by imposing taxes on import sugar and consuming sugar, but it will be difficult after the conclusion of TPP. For this reason, all processes on sugar cane cultivation and sugar production have to be studied to improve the value of cane cultivation.

At sugar cane mill, there appear many amounts of uncrystallized sugar waste named molasses during the raw sugar production. The amount accounted for ca. 22,000ton which correspond to ca.25% of crystallized sugar product of 88,000ton in Okinawa prefecture in 2010. This molasses contains ca.40% of sugars (sucrose, fructose, glucose), so it is very good stock for ethanol fermentation. However, since the transportation cost from islands to the Mainland is so high, the market price is very low as about ¥1,500 per ton while standard

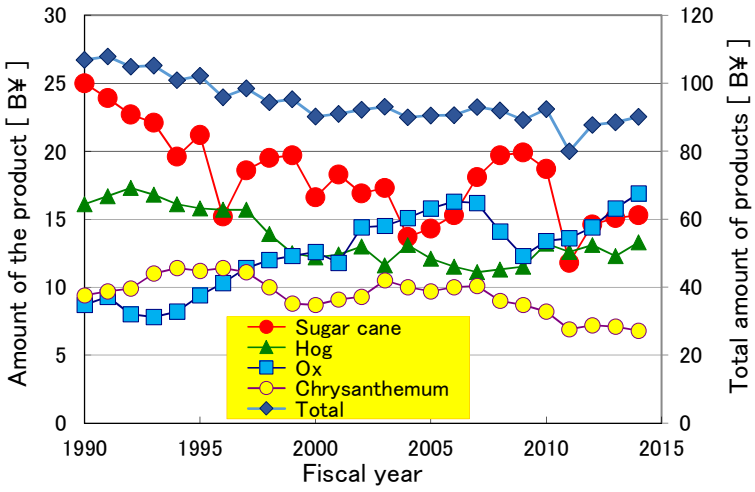


Fig. 1. Agricultural receipts in Okinawa prefecture.

price of raw sugar was around ¥250,000 per ton in 2002. Therefore, the contribution to the total sales of mill factory was only less than 0.2%.

Authors have been trying to use molasses as stock for hydrogen production by fermentation to use hydrogen for the fuel of fuel cell vehicle or electric power generator. Because in islands, electric power is mainly supplied by thermal power generation using diesel oil, while the use of fossil fuel is requested to reduce so as to stay the global warming. In view of this situation, we made a small pilot plant for hydrogen production from molasses at Itoman city in Okinawa. In this paper, we report the result of its operation.

Photo 1. Small pilot plant set at Itoman city in Okinawa. The top tank is the fermentor with 200L volume.

2. A pilot plant for experiment and experimental condition

Clostridium sp. strain HN001[1] was used in this experiment. Since the bacterium multiplies very rapidly under sufficient nutrients and substrates, it produced hydrogen at a speed of 5L-H_2/L-culture·h under the condition of very short hydraulic retention time (HRT) as 1hour by laboratory scale experiments[2]. To verify the productivity in a large scale, a small scale pilot plant that will produce 22m^3 hydrogen by fermenting 200kg of molasses at a day was made at Itoman city by the subsidy from Okinawa Industry Promotion Public Corporation[3]. The volume of fermenter is 200L with a fermentation capacity of 160L (Photo 1).

The workout was operated by replacing 80L waste liquid with 80L new culture from 160L. The fermentation temperature was kept at 40°C and the cultural pH 5.5. The results is shown in Figure 2. Since the sugar concentration was set at 3.5% by program, a biogas of 1,400L volume was expected to be produced a day from the calculations. There was a flow out trouble on feed at the start-up day and a control miss of cultural pH at the third day, perfect data therefore could not get, but the satisfactory results were taken in the graph. The concentration of hydrogen was 53% of the biogas.

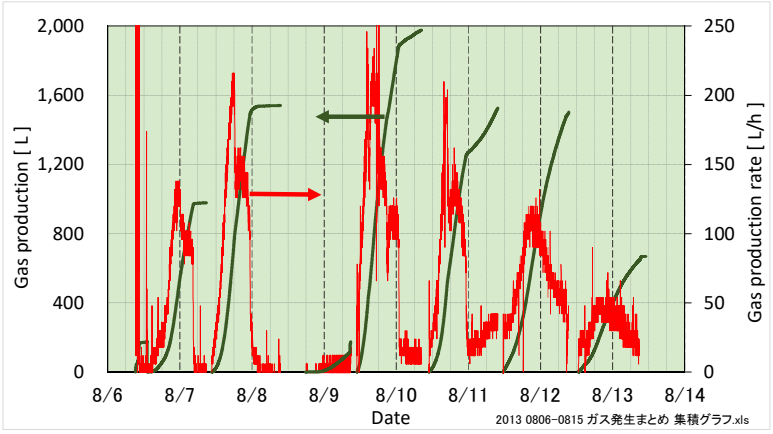


Fig. 2. Results of the workout of the pilot plant by fed batch operation with molasses.

3. Results of continuous operation of the pilot plant

3.1 In case of the bacterium *Clostridium* HN001

Figure 3 shows the results of the continuous operation of fermentation by *Clostridium* strain HN001 with molasses[4]. The operation continued almost three months while several times it stopped by pomp accidents. To increase the cell concentration, the fed batch operation was adopted for 10 days at the beginning, then switched to the continuous operation.

From 69th day, the operation was changed to the fed batch for 18 days. The gas yield from molasses during this term became around 200L from 1L of molasses, as almost double yields compared to the continuous operation.

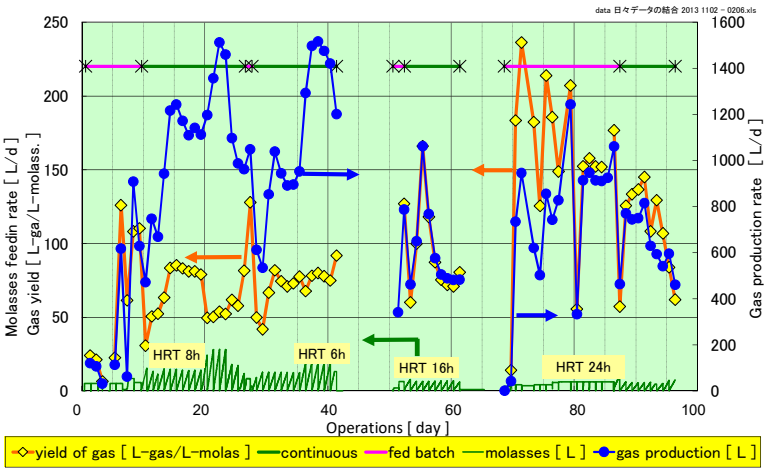


Fig.3. Results of continuous operations by the HN001.

3.2 In case of a newly found microflora

To reduce the amount of sodium hydroxide for pH controlling, a new microflora was hunted and found.

Figure 4 shows the results of the first fed batch operations by the newly found microflora. The hydrogen productivity of the microflora was examined under three kinds of hydraulic retention time (HRT) of the feed such as 6, 12 and 24hours. The hexose concentration of feed was set at 2%, but it couldn't be kept rigidly because of the viscosity of molasses. The rate of biogas production and the yield of biogas in terms of hexose at HRT 6, 12 and 24h were ca. 100L/h and ca. 3.0mol/mol, ca. 75L/h and ca. 4.6mol/mol, and 60L/h and ca. 6.6 mol /mol respectively. The only care was that the biogas consisted of H_2 and CO_2 contained hydrogen only ca. 30% while 52% at 3L bench scale fermenter experiment. However, since the hydrogen yield at 24hr-HRT is estimated at ca. 2.0mol-H_2/mol-hexose, this flora will be a hopeful microflora.

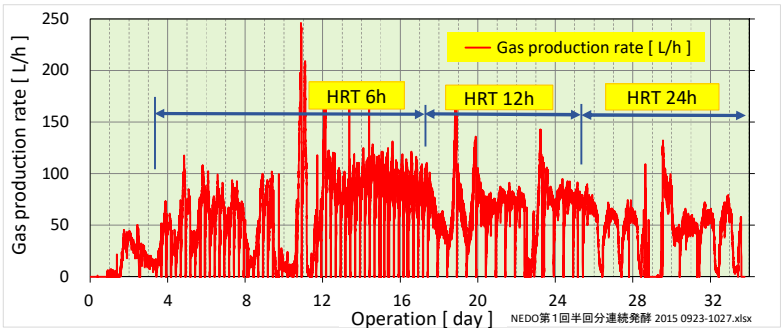
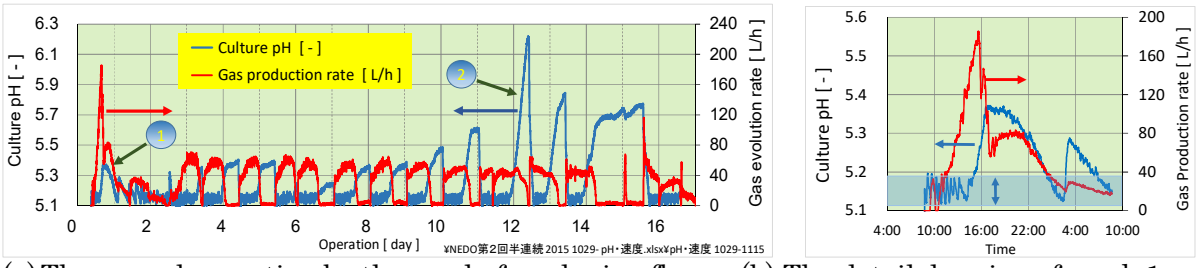


Fig. 4. Gas production rates at each HRT operation.

3.3 pH rising phenomena at fed batch operations by a newly found microflora

Figure 5 shows gas production rates and culture pH at the second fed batch operation by the newly found microflora. At this operation, a distinctive phenomenon appeared on culture pH. The pH was controlled to keep at the range from 5.1 to 5.2 by adding NaOH. But the flora often went over the upper limit pH of its own accord. As clearly shown in Fig.5 (b), the rising



(a) The second operation by the newly found microflora. (b) The detail drawing of mark 1.

Fig. 5. Culture pH rising appeared at fed batch operation by the newly found microflora.

appeared while bacteria producing gas actively.

To make clear the reason, liquids of fermenter were sampled every one hour. The analyses by liquid chromatography cleared up very distinctive transition of metabolite's concentrations as seen in Fig. 6. It showed that the concentration of lactate decreased along with the pH increase, and in contrast to lactate, the concentration of butyrate increased. The relation between the concentration movement of lactate and butyrate is such that the twice amount of the concentration increment of butyrate is equal to the single amount of the concentration decrement of lactate. It is expressed by the following chemical equation,

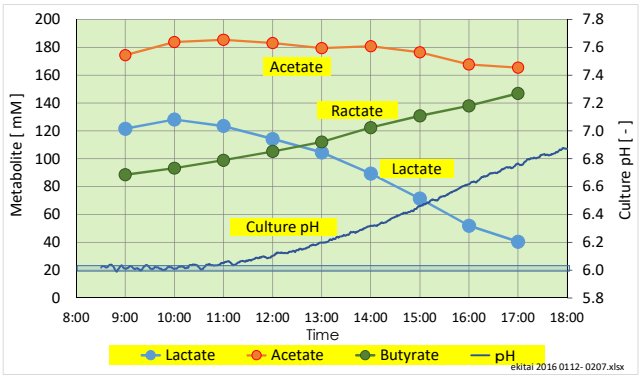


Fig. 6. The change of metabolite's concentrations at the pH rising period of culture.

$$2CH_3CHOHCOOH \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2.$$

4. Discussion

Japanese car makers such as Toyota and Honda have started selling fuel cell cars. By this circumstance, mass-productive fuel cell becomes easy to get. The power of fuel cell for car has more than 100kW and the energy conversion efficiency is nearly 60%, therefore if bio-hydrogen is accessible to fuel cells for car, local power will be generated conveniently from the renewable hydrogen. For example, ca. 440MWh will be producible from the molasses of Minamidaitou island, Okinawa (details are described in the reference 2). This amount corresponds to nearly 5% of the whole power demand at the fiscal year of 2009 in the island and to one month of home use. Production of molasses is short as 3 months in a year, if molasses are used throughout the year, volume of the fermenter is small enough only $10m^3$, therefore fermentative hydrogen production will be a very effective renewable energy production for the local spot.

Acknowledgements

On this study, the pilot plant could be made by the subsidy from Okinawa Industry Promotion Public Corporation and the experiments by using the newly found microflora were accomplished by the grant from the New Energy and Industrial Technology Development Organization (NEDO). We would like to express to those organizations our deepest gratitude for giving us their supports.

References

1. Nishiyama, H and Tanisho, S. Fermentative Hydrogen Production by a Newly Isolated Mesophilic Bacterium HN001 16th World Hydrogen Energy Conference, Lyon, France, in CD ROM, (2006).
2. Yasuda, K. Biological hydrogen production from food waste by fermentation, Doctoral thesis, Yokohama National University, (2009).
3. Tanisho, S., Hayashi, T., Fujisawa, S., Hasegawa, Y. and Gontani, S. Fermentative Hydrogen Production from Molasses by a Pilot Plant Constructed in Okinawa, Report I, Proc. 33th Conf. Hydrogen Energy Systems Society Japan, (2013).
4. Tanisho, S., Hayashi, T., Fujisawa, S., Miyahira, H., Gushi, K. Fermentative Hydrogen Production from Molasses by a Pilot Plant Constructed in Okinawa, Report II, Proc. 34th Conf. Hydrogen Energy Systems Society Japan, (2014).
5.