Biohydrogen Production from Combined Dark-photo Fermentation under a high Ammonia Content in the Dark Fermentation Effluent

C.-Y. Chen, Y.-C. Lo, K.-L. Yeh, J.-S. Chang

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 2: Hydrogen Production Technologies – Part 1
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-2
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-652-1

A Pilot Study of Nitrogen Composition and Effect on Biohydrogen Production

Sheng-Shung Cheng, Energy and Environmental Laboratories, Industrial Technology Research Institute, 1955, sec 4, Chung Hsing Rd., Chungtung, Hsinchu, 31040, Taiwan (R.O.C.)
Ming-Der Bai, **Yu-Chieh Chao**, **Yun-Huin Lin**, Department of Environmental Engineering, National Cheng Kung University, No.1, University Rd., East District, Tainan City 701, Taiwan (R.O.C.)

1 Introduction

Biohydrogen is a potential technology that converts industrial wastes into hydrogen and simple fatty acids. However, there has been only little research working on continuous operation in large scale. Ren et al, [2006] [1] operated a 1.48 m^3 pilot-scale bioreactor using molasses as substrate. Hydrogen can be recovered and the maximum hydrogen production rate was 5.57 m^3-H_2/m^3-reactor/d. For the lack of performances data of biohydrogen system applying on industrial wastes, commercial popularization is very difficult. To improve this situation, a biohydrogen pilot plant with a 1,000 L working volume was built on an industrial site. This study was, therefore, carried out to collect operational parameters and performance indexes for scaling up.

It is universally known that carbohydrate was most suitable for hydrogen production, and most feedstock used in biohydrogen fermentation containing nitrogen source to enhance growth and activity of hydrogen-producing bacteria. However, few studies paid their attention to the important and effects of nitrogen on hydrogen fermentation. Yokoi [1995] [2] notice that polypepton could enrich hydrogen production, but it would react with glucose in high temperature to produce some chemical to inhibit hydrogen production. Ueno [2001] [3] commented the different bacteria community caused by different nitrogen source. Nitrogen source influents the cell growth and hydrogen production of hydrogen-fermenting bacteria.

2 Materials and Methods

A continuously flow biohydrogen reactor with a working volume of 1 m^3 was used in this study. Total volume of the reactor was 1.6 m^3 and sucrose and fodder wastes were used as substrates.

The feeding stuff was made of 1 portion of fodder waste and 4 portions of sucrose, and the organic concentration of the substrate was about 10 g-COD/L. Different hydraulic retention time (HRT) was controlled for different OLR operation.

The biogas produced from the reactor was measured by a gas meter continuously; biogas was collected by water displacement method then analyzed by a gas chromatograph (Model 6890N, HP) equipped with a thermal conductivity detector (TCD). The concentration of sucrose was determined by phenol-sulfuric method [Herbert et al., 1971 [4]]. Water quality

analyses were conducted according to the procedures described in the Standard Method 19th edition [APAH 1995 [5]].

3 Results and Discussion

A biohydrogen pilot plant was built in an industrial field, which was consisted of an acidogenesis tank for hydrogen production and a methanogenesis tank for methane production by using several industrial wastes or wastewater as raw materials. During the decomposing process of the raw materials, hydrogen and methane were produced. The units of the process were adjusted and the hardware facilities were improved during the operation time. In the start-up phase, sucrose and fodder waste were used as substrates for microbial propagation. The objective of this phase was to make hydrogen-producing bacteria active so as to endure higher volumetric organic loading in the next phase. In the second phase, volumetric organic loading rate was controlled at 3.3 kg-COD/m^3-day initially, then the loading was increased to 6.7 kg-COD/m^3-day. By applying the two-phase organic loading control, a high hydrogen yield of 120~133 L H_2/kg-COD was achieved. However, the fodder waste in the feedstock limited organic nitrogen, which cannot supply sufficient nitrogen for microbial growth.

In this case study, fodder wastes was the only nitrogen source in the substrate, which used only as assimilation for bacteria propagation. The nitrogen content in the fodder waste was around 3 to 4%. Therefore, the nitrogen supply in the total feedstock was about 1.2-1.6%. It was too little for the hydrogen production bacteria to grow under the OLR of 6.7 kgCOD/m^3/d. Besides, the amount of total Kjeldahl nitrogen in the reactor decreased gradually to 20 mg-N/L, which was only enough for composing a biomass amount about only 160 mg/L. Gradually, hydrogen yield was reduced in the condition of nitrogen lacking, and the profile of valitile fatty acids was shifted to a pathway which is unfavourable for hydrogen producing.

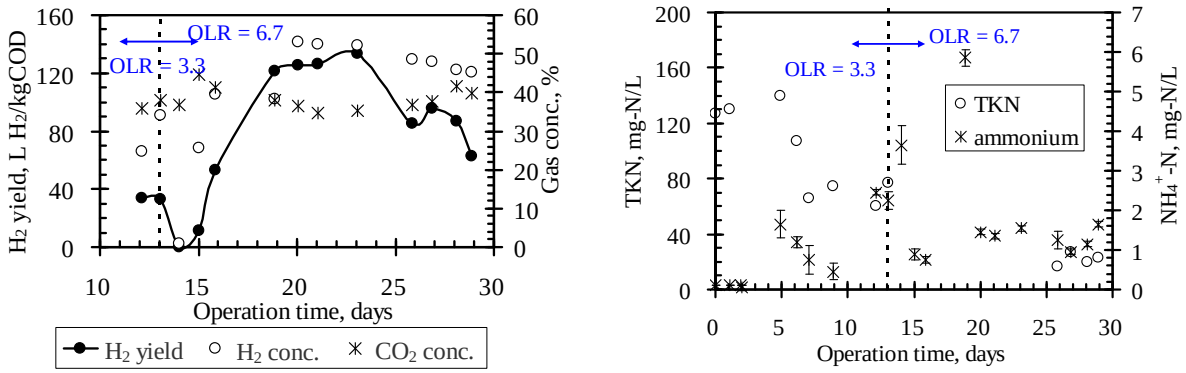

Figure 1: The hydrogen production (left) and nitrogen concentration (right) profile in the biohydrogen fermentor.

To resolve the problem, urea was added to make up the shortage of nitrogen content in the substrate. After urea was added, hydrogen yield was recovered to 100 L H_2/kg-COD and the fermentation pathway was shifted back to the desired butyrate/acetate-leading process. Although the hydrogen yield was recovered, the troublesome scum problem was caused by rapid hydrogen production rate. The foam can overflow the gas purifying tank, obstruct the

gas tube, and nullify the gas flow meter. Several low hydrogen production data obtained in the urea addition duration was caused by the troublesome scum problem. However, the substantially increase in the biohydrogen fermentation byproducts, acetate and butyrate indicated that the metabolism pathway in the fermentor had shifted to the hydrogen production metabolism.

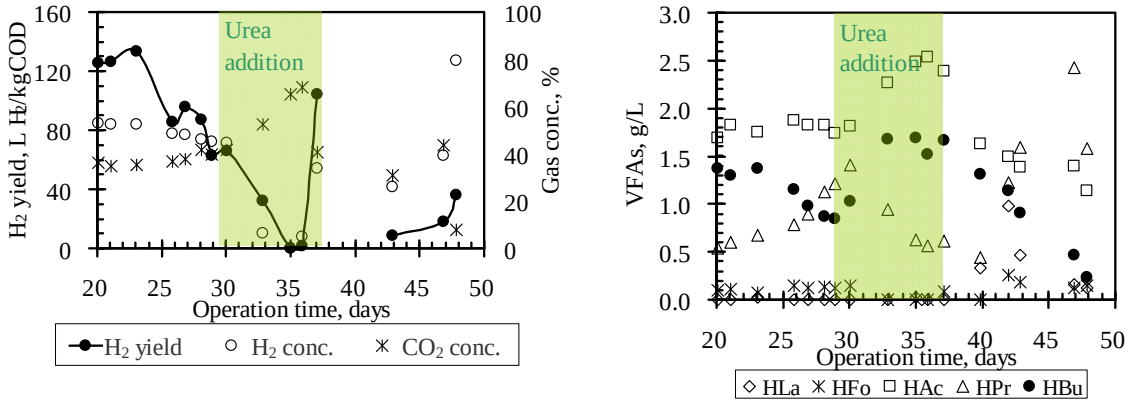

Figure 2: The hydrogen production (left) and fatty acid byproducts (right) profile in the biohydrogen fermentor operated with and without extra nitrogen addition.

Because of the hydrogen gas meter nullified and biomass washed out by the scum problem, the urea addition was broken off after 8 days, and the hydrogen, acetate and butyrate production decreased immediately. The metabolism pathway in the fermentor had shifted away from the hydrogen production metabolism.

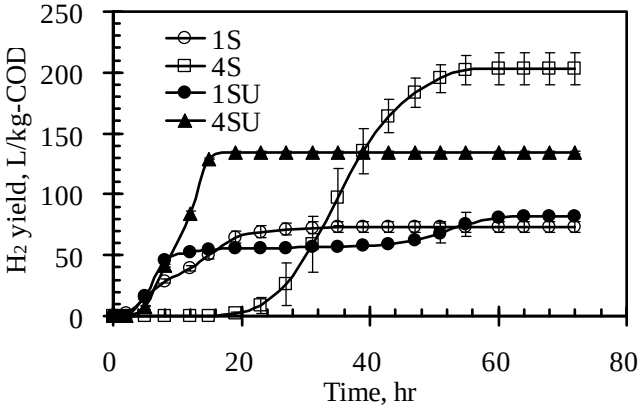

Figure 3: Hydrogen production profile in the batch hydrogen fermentation. (U: urea extra addition; 4S : 4 g/L sugar +1 g/L waste fodder; 1S : 1 g/L sugar +4 g/L waste fodder)

A batch test was conducted to investigate this nitrogen insufficient phenomenon. The results (Figure 3) showed that urea addition can greatly shorten the lag phase and increase the maximum hydrogen production rate. However, urea addition also limited the hydrogen recovery at high sucrose content. This may result from the energy consumption for bacteria

growth, and therefore shifted the electron flow from hydrogen to cell division. Under continuous operation, with limit organic nitrogen the growth rate of bacteria was low and can't be retained in the reactor resulting in a decline in hydrogen production.

4 Conclusion

Used as feedstock in hydrogen fermentation, waste fodder could not provide enough nitrogen for cell growth, which causes biomass concentration decreasing and shifting the metabolism pathway away from biohydrogen production. The best hydrogen production was caused in the exponation phase, the cell growth rapidily phase. However, the batch biohydrogen fermentation test results showed that urea addition also limited the hydrogen recovery that may result from the energy consumption for bacteria growth.

Acknowledgements

The authors gratefully acknowledge financial support by Taiwan's Bureau of Energy, Ministry of Economical Affairs.

References

[1] Ren N., J. Li, B. Li,Y. Wang, S. Liu. "Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system", Int. J. of Hydrogen Energy, 31:2147 – 57. 2006.

[2] Yokoi, H., Ohkawara, T., Hirose, J., Hayashi, S. and Takasaki, Y. (1995) Characteristics of Hydrogen Production by Aciduric Enterobacter aerogenes Strain HO-39. Journal of Fermentation and Bioengineering, 80(6), 571-574

[3] Ueno, Y., Haruta, S., Ishii, M. and Igarashi, Y. (2001) Microbial community in anaerobic hydrogen-producing microflora enriched from sludge compost. Applied Microbiology and Biotechnology 57, 555-562.

[4] Herbert D., P. J. Philipps and R. E. Strange, "Carbohydrate analysis," Methods Enzymol., 5B, 265-277. 1971.

[5] Standard Method for the Examination of Water and Wastewater, 19 th ed. APAH, Washington, DC. 1995.