RELATION BETWEEN H_2 PRODUCTION AND ORGANIC ACID FORMATION IN HYDROGEN FERMENTATION WITH RICE BRAN

[1]ZHIXUAN FANG, [2]YU-ICHI UCHIDA

Graduate School of Engineering, Nippon Institute of Technology, JAPAN 3458501
E-mail: [2]yuichi.uchida@nit.ac.jp

Abstract - The relation between H_2 production and organic acid formation during anaerobic hydrogen fermentation using rice bran was investigated in a laboratory experiment. 50 g of rice bran that had been heat-treated at 90°C for 30 minutes was added to 1 L of purified water and kept at 40°C, without addition of particular inoculum. At the early stage of fermentation, relatively large amount of mixed gas of H_2 and CO_2 was generated and lactic acid was mainly produced. Subsequently, the generated gas tended to decrease over time followed by the decrease of lactic acid and the accumulation of acetic and butyric acids. The initial H_2 generation rate and H_2 / CO_2 ratio in the generated gas tended to be slightly higher for the experiments carried out under pH controlling to 6. Such result would suggest that pH influences microbial reaction and resulting organic acid formation during fermentation, potentially playing an important role in hydrogen production.

Keywords - Hydrogen Fermentation, Hydrogen Gas, Rice Bran, Organic Acid, Ph.

I. INTRODUCTION

Currently, most hydrogen production comes from fossil fuels such as coal or natural gas. From the perspective of CO_2 reduction, utilization of hydrogen for energy source or reductant. In such viewpoint, H_2 production with water electrolysis using green electricity is desirable, but there are concerns about mismatch between the supply and the demand of H_2. Sustainable H_2 production from biomass as a raw material has the potential to be a promising supplemental way [1-18].

Among a large variety of biomass, rice bran has been massively generated through rice cultivation especially in many Asian countries. Some of them are served to produce rice oil or fertilizer, however, it is not fully used and is disposed or incinerated in most other cases.

Some papers showed H_2 production through anaerobic hydrogen fermentation with rice bran. In some of them, particular inoculum is added to de-oiled rice bran[19], while the method without using inoculum has not been reported.

The present authors are paying attention to the latter way, which would be preferable considering a feasibility for actual operation of H_2 production. In this paper, we investigated the effect of pH on hydrogen fermentation using rice bran as a raw material.

II. EXPERIMENTAL ASPECTS

Schematic diagram of the experimental apparatus is shown in Fig. 1. Separable flask with a lid was placed in a water bath equipped with a magnetic stirrer. Three openings on the lid were provided for ; a glass tube with a three-way stopcock for sampling fermentation liquid, a pH probe, and an inlet for KOH solution and a gas collection port. Each opening secured with a rubber stopper.

Raw material (rice bran) was heat-treated at 90°C for 30 minutes prior to the experiment, and then was added with purified water in a separable flask. No particular bacteria or microorganism are added. At the beginning, air in the freeboard was replaced by nitrogen gas. During fermentation, pH inside the flask was monitored using a pH probe. The liquid was maintained at a specified pH with a pH controller connected to the probe by adding 1 M KOH solution.

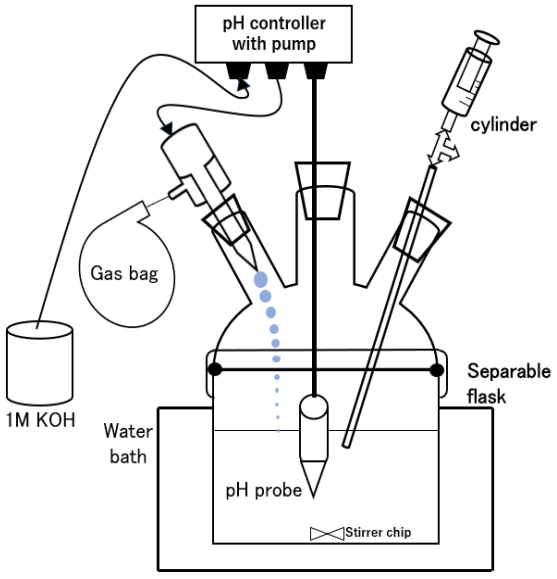


Fig.1 : Schematic illustration of experimental setup.

The gas generated was collected in gas bags. The fermentation liquid was sampled using a cylinder through the glass tube dipped in the liquid. At each sampling, small amount of nitrogen gas was introduced to expel stagnant liquid in the glass tube. The gas composition was analyzed with a gas chromatograph. The organic acid concentration in the fermentation liquid was analyzed with HPLC.

The main experimental conditions are shown in Table 1. 50g of rice bran was added into 1L of purified water to prepare a testing liquid. The liquid temperature was kept at 40℃. In some experiments the pH of the liquid was controlled at 6.

Pre-treatment	Heat treatment at 90°C for 30 minutes
Testing liquid	Rice bran 50g + Purified water 1L
Temperature	40°C
pH	Non-controlled, 6

Table 1 Experimental conditions.

III. EXPERIMENTAL RESULTS

Fig. 2 shows an example of pH change with time under uncontrolled pH conditions. pH decreased from an initial value near 7 to a final value around 4. Stepwise change was observed initially, with differing rates between pH 7~6 and pH 6~5. After 1500 min, the pH remained nearly constant.

Fig. 3 shows the pH change with time under pH controlled to 6. The pH began to decrease at approximately the same time as under uncontrolled conditions, and pH control was initiated after reaching the target pH. Although pH temporarily increased in some periods, it was stably maintained within a desired level through the experiment.

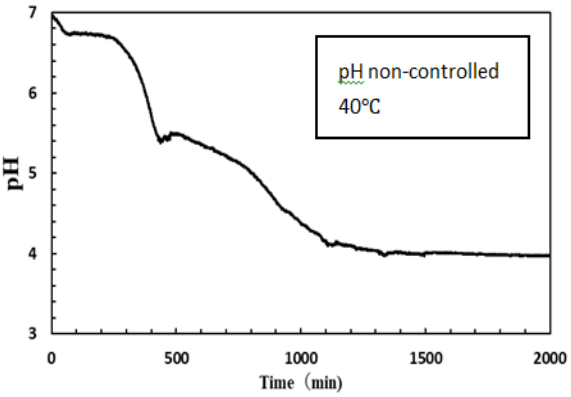


Fig. 2 : Change of pH with time (pH non-controlled condition)

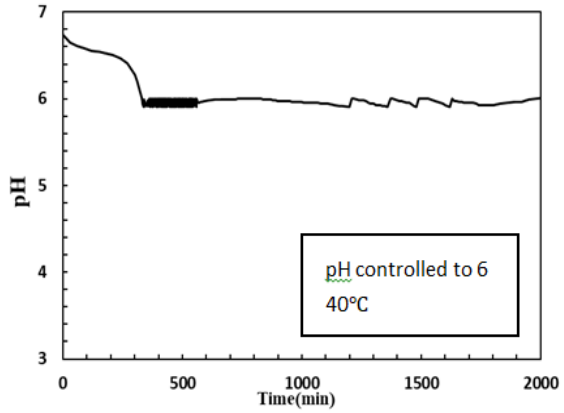


Fig. 3 : Changes of pH with time (pH controlled to 6)

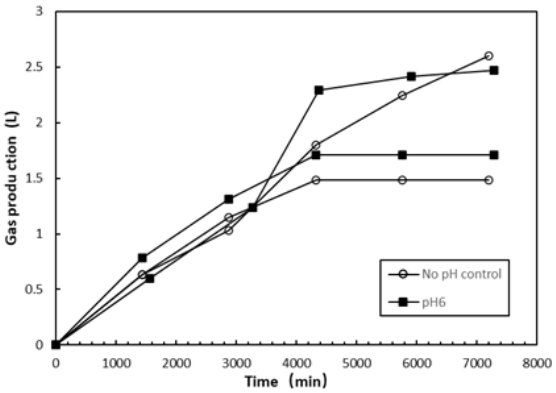


Fig 4 : Cumulative gas production with time.

During hydrogen fermentation, H_2 and CO_2 is generated at the same time. Fig. 4 shows the changes in cumulative gas production with and without pH control. In both conditions, cumulative production increased at least three days. Beyond three days, in some cases the gas production kept increasing for a longer time, and in another cases it stopped. The cumulative gas generation in the experimental duration is macroscopically not so different with respect to pH controlling, however, the gas generation rate in early stage was slightly higher for the pH 6 condition compared to the uncontrolled condition.

Considering glucose as an example of a starting material for hydrogen fermentation, the overall reaction may be shown by the following equation.

$$C_6H_{12}O_6 + 2H_2O = 4H_2 + 2CO_2 + 2CH_3COOH$$

This equation gives the ratio of H_2 against CO_2 (referred as hydrogen ratio) of 2. Fig. 5 shows the relationship between H_2 generation rate and CO_2 generation rate for each period during gas sampling. Those are positively correlated, and the hydrogen ratio for each data point can be evaluated in terms of the straight lines with guide values. Although there are scatterings of the data, the data points at lower CO_2 generation rate correspond to relatively larger hydrogen ratio, while the data at higher CO_2 generation rate show relatively smaller ratio.

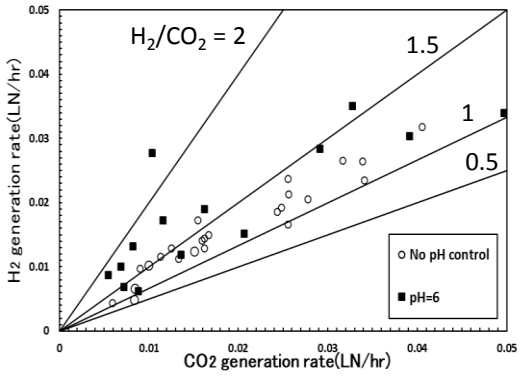


Fig 4 : Relationship between H_2 generation rate and CO_2 generation rate.

With respect to pH controlling, the hydrogen ratio for the pH 6 condition seems relatively larger regarding to the presence of some high-leveled data, compared to the uncontrolled condition. It should be mentioned, here at this point, that most of the data in this experiment correspond to the hydrogen ratio less than 2 derived from the above equation. This would suggest a complex nature of the hydrogen fermentation.

Fig. 6 is an example of the change of organic acid concentration with time under the uncontrolled pH conditions. On the first day of fermentation the concentration of lactic acid increased steeply, but it decreased afterwards. On the other hand, the concentration of acetic acid and butyric acid gradually increased. Such changes would support again complex reactions in the fermentation. For the pH 6 condition, the overall trend was similar to in the figure.

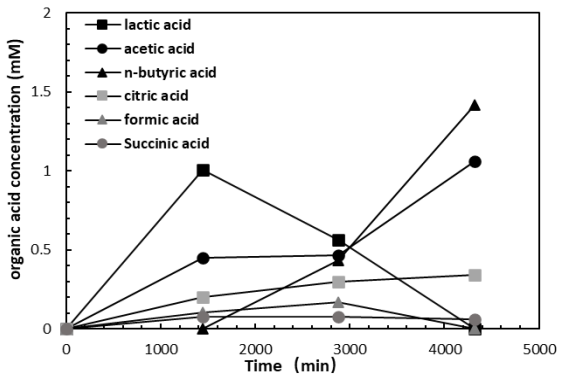


Fig. 6 : Change of organic acid concentrations with time.

IV. DISCUSSION

Based on the cumulative hydrogen production and the changes of organic acid concentrations with time, it is considered that the pathway for lactic acid fermentation, where substances in rice bran are reduced to lactic acid through glycolysis, was dominant in the initial stage. This would likely lead to an increase in H_2 production rate. As fermentation proceeds, lactic acid decreases and gives acetic acid and butyric acid would, derived from lactic acid. A decrease in the hydrogen production rate was observed at this stage so that some turning point of reaction may exist.

As can be seen in Figures 5 and 6, the better influence of pH control might be expected. This suggests that a suitable pH may exist for microbial metabolic behaviour during fermentation. Through optimization of such behaviour, the patterns of each organic acid generation could reflect the better pathways for promising hydrogen production.

V. CONCLUSION

Hydrogen fermentation using rice bran was investigated as a sustainable and supplemental way of H_2 production. A laboratory experiment was carried out focusing on the relation between H_2 production and organic acid formation during anaerobic hydrogen fermentation using rice bran.

At the early stage of fermentation, relatively large amount of mixed gas of H_2 and CO_2 was generated and lactic acid was mainly produced. Subsequently, the generated gas tended to decrease over time followed by the decrease of lactic acid and the accumulation of acetic and butyric acids. This would suggest a complex nature of the fermentation.

The initial H_2 generation rate and H_2 / CO_2 ratio in the generated gas tended to be slightly higher for the experiments carried out under pH controlling to 6. Such result would suggest that pH influences microbial reaction and resulting organic acid formation during fermentation, potentially playing an important role in hydrogen production.

REFERENCES

[1] S. K. Khana et al.: Int. J. Hydrogen Energy, 29 (2004), pp.1123 – 1131.
[2] D. B. Levin et al. : Int. J. Hydrogen Energy, 29 (2004), pp. 173-185.
[3] Y. Kawagoshi et al, : J. Bioscience Bioengineering, 100 (2005), pp.524–530.
[4] I. Valdez-Vazquez et al. : Int. J. Hydrogen Energy, 30 (2005), pp. 1383 – 1391.
[5] W. H. Chena et al. : Int. J. Hydrogen Energy, 31 (2006), pp.2170 – 2178.
[6] D. das et al. : Int. J. Hydrogen Energy, 33 (2008), pp.6045-6057.
[7] Y. Akutsu et al. : :J. Jpn. Biological Soc. Water Waste, 44 (2008), pp.57.
[8] D. H. Kim et al. : Enzyme and Microbial Technology, 45 (2009), pp.181–187.
[9] D. H. Kim et al. : Bioresource Technology, 102 (2011), pp.8646–8652.
[10] P. C. Hallenbeck et al. : Bioresource Technology, 110 (2012), pp.1-9.
[11] G. Grause et al. : Int. J. Hydrogen Energy, 37 (2012), pp.16967-16973.
[12] G. De Gioannis et al. : Waste Management, 33 (2013), pp.1345-1361.
[13] K. Tanaka et al. : Journal of Computer Aided Chemistry, 18 (2017), 42.
[14] O. García-Depraect et al. : Bioresource Technology, (2020), 124595.
[15] J.R. Banu et al. : Bioresource Technology, 298 (2020), 122378.
[16] E. Castro et al. : Frontiers in Energy Research, 9 (2021), pp.111.
[17] A. Ohnishi et al. : Bioresource Technology, 343 (2022), 126076.
[18] T. Noike et al. : Int. J. Hydrogen Energy, 27 (2002), pp.1367-1371..
[19] N. F. Azman et al. : Int. J. Hydrogen Energy, 4 (2016), pp.145-156.

★★★