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Continuous Hydrogen Production from Starch by Fermentation

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Abstract

This study was investigated the effect of hydraulic retention time (HRT) on hydrogen production rate, hydrogen yield and the production rate of volatile fatty acid. The experiment was performed in a continuous stirred tank reactor (CSTR) with a working volume of 1 L by using a *Clostridium* sp. The temperature of the CSTR was regulated 37 °C. The pH was controlled 6.0 by the addition of 3 M of NaOH solution. Starch was used as the carbon source with the concentration of 30 g L^{-1}. Hydrogen production rate increased from 0.9 L-H_2 L-culture^{-1} h^{-1} to 3.2 L-H_2 L-culture^{-1} h^{-1} along with the decrease of HRT from 9 h to 1.5 h. Hydrogen yield decreased at low HRT. The major volatile fatty acids are acetic acid, butyric acid and lactic acid. The production rates of acetic acid and butyric acid increased along with the decrease of HRT. On the other hand, the rate of lactic acid was low at high HRT while it increased at HRT 1.5 h. The increase of the production rate of lactic acid suggested one of the reasons that hydrogen yield decreased.

1 Introduction

Biological H_2 production has been studied widely. Fermentative H_2 production, one of the biological H_2 productions, is promising compared with another biological H_2 production by photosynthetic organisms because it is possible to produce H_2 all day long without light. Continuous H_2 production by fermentation has been studied. There are some problems for the commercialization. One of the problems is H_2 productivity such as production rate and yield of H_2. Wu *et al*. reported that H_2 production rate reached 15 L L-culture^{-1} h^{-1} by using silicone immobilized sludge with self-flocculated under the condition of sucrose concentration 40 g-COD L-culture^{-1} and HRT 0.5h [1]. H_2 fermentation utilizes various sources such as wastewater [2], molasses [3] and palm oil mill effluent [4]. *Thermotoga maritime* attained 4 mol-H_2 mol-hexose^{-1}, the theoretical maximum yield of H_2, at 80 °C by batch cultivation, while H_2 production rate was 10 mmol L-culturee^{-1} h^{-1} [5]. However, almost all the H_2 yield reported is lower than 4 mol-H_2 mol-hexose^{-1}.

In this study, continuous H_2 production from starch was examined to investigate the effect of HRT on H_2 production.

2 Materials and Methods

Clostridium sp HN001 was used in this study. This bacterium was found by screening and isolated [6].

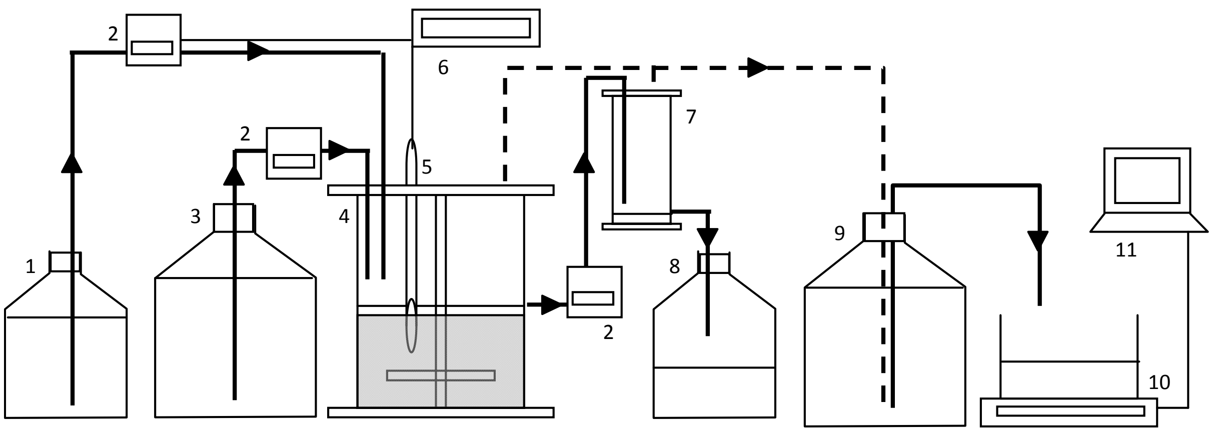
The culture medium contained starch 30.0 g, casamino acids 10.0 g, yeast extract 10.0 g, L-cysteine hydrochloride 0.3 g, thioglycolic acid 0.3 g $FeCl_2$ 0.1 g per 1 L of ion exchanged water. The culture was sterilized at 121 °C, 15 minutes.

Figure 1 shows the outline of experimental apparatus. A 1.0 L continuous stirred tank reactor was used. The volume of culture liquid was 0.5 L. The temperature was maintained at 37 °C. The pH was automatically regulated by the addition of 3 M of NaOH solutions. The culture was stirred by a magnetic stirrer. The liquid level was controlled by using micro tube pomp. Feeding the medium at HRT 9 h started after appropriate period of batch fermentation. HRT was decreased from 9 h to 1.5 h when a steady state reached.

Product gases were collected in a bottle filled with 1 M of NaOH solution. The NaOH solution was replaced in accordance with the volume of H_2 and the replaced volume was measured by an electric scale.

The gases were analyzed by a gas chromatograph (SHIMADZU).

VFA was analyzed by a high performance liquid chromatograph (HITACHI, Ltd 655A), equipped with refractive index detector. The assay was analyzed by a packed column for organic acid analysis (HITACHI Chemical Co., Ltd. GL-C610-S). The carrier liquid was 0.1 % phosphoric acid at flow rate of 0.5 ml/min.



1. 1M NaOH tank 2. Peristric pump 3. Feed tank 4. Continuous stirred tank reactor 5. pH electric pole 6. pH controller 7. Gas liquid separator 8. Effluent tank 9. Gas tank 10. Electric scale 11. PC

Figure 1: The outline of experimental apparatus.

3 Results and Discussions

Figure 2 shows the effect of HRT on H_2 production rate and H_2 yield. H_2 production rate was 0.9, 1.2, 1.9 and 3.2 L L-culture^{-1} h^{-1} at HRT 9.0, 6.0, 3.0 and 1.5 h, respectively. H_2 yield was 2.0 mol mol-hexose^{-1} at HRT 9.0 and 6.0 h. However, it decreased to 1.5 and 1.3 mol mol-hexose^{-1} when HRT was shortened to 3.0 and 1.5 h, respectively.

Figure 3 shows the effect of HRT on butyrate, acetate and lactate production rate. Acetate production rate was 4.9, 7.3, 12.2 and 24.7 mmol L-culture^{-1} h^{-1} and butyrate production rate was 9.3, 13.4, 19.7, 46.1 mmol L-culture^{-1} h^{-1} when HRT was 9.0, 6.0, 3.0 and 1.5 h, respectively. On the other hand, lactate production rate was relatively low when HRT was shortened from 9.0 to 3.0 h. However, it increased to 15.8 mmol L-culture^{-1} h^{-1} at HRT 1.5 h. The decrease of H_2 yield at short HRT has been reported [7, 8, 9]. As seen in the following equations from glucose by H_2 producing bacteria under anaerobic conditions, acetate and butyrate were produced with H_2 and lactate was produced without H_2.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$
$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2CO_2 + 2H_2$$
$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$$

One of the reasons that H_2 yield decreases seems lactate production. Wang *et al*. reported that H_2 yield decreases with the addition of acetate [10]. Zheng *et al*. also reported that H_2 yield decreases with the addition of butyrate [11]. The metabolic shifts cause the decrease of H_2 yield in this study. H_2 partial pressure inhibits H_2 productivity [12]. Mizuno *et al*. achieved a 68% increase of H_2 yield by N_2 sparging [13]. Kim *et al*. reported that H_2 yield was improved from 0.77 mol mol-hexose^{-1} to 1.68 mol mol-hexose^{-1} by gas sparging of N_2 and CO_2, respectively [14]. Therefore continuous H_2 production at short HRT with the decrease of H_2 partial pressure would be future work to improve H_2 productivity.

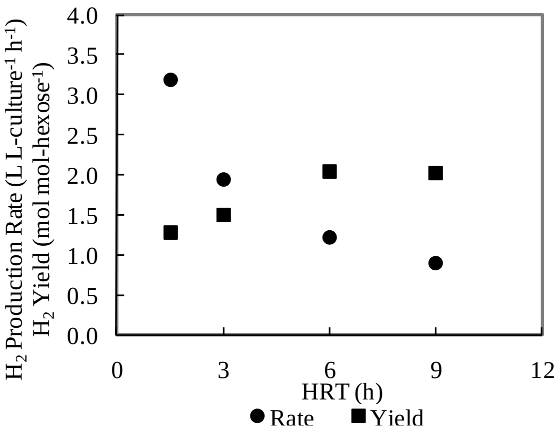


Figure 2: The effect of HRT on H_2 production rate and H_2 yield.

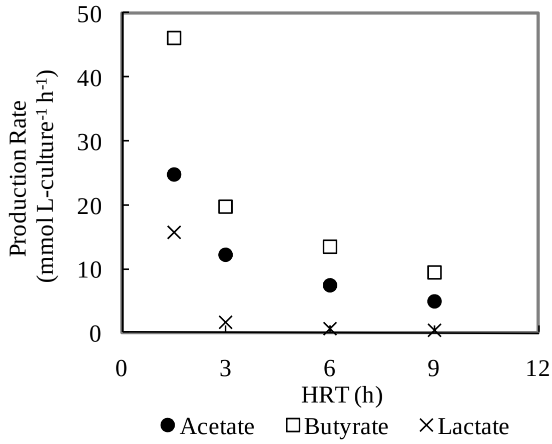


Figure 3: The effect of HRT on VFA production rate.

4 Conclusions

In this study, the following conclusions can be drawn:

- H_2 production rate increased from 0.9 to 3.2 L L-culture^{-1} h^{-1} when the HRT was shortened from 9.0 to 1.5 h.
- H_2 yield was 2.0 mol mol-hexose^{-1} at HRT 9.0 and 6.0 h and decreased to 1.3 mol mol-hexose^{-1} along with the decrease of HRT from 6.0 to 1.5 h. The reason was the shift of metabolites.

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