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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-culture\(^{-1}\) 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 H₂ 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.

Figure 2 shows the effect of HRT on H₂ production rate and H₂ yield. H₂ 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. H₂ 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 \(\text{H}_2\) yield at short HRT has been reported [7, 8, 9]. As seen in the following equations from glucose by \(\text{H}_2\) producing bacteria under anaerobic conditions, acetate and butyrate were produced with \(\text{H}_2\) and lactate was produced without \(\text{H}_2\).

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} & \rightarrow 2\text{CH}_3\text{COOH} + 2\text{CO}_2 + 4\text{H}_2 \\
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow \text{C}_3\text{H}_7\text{COOH} + 2\text{CO}_2 + 2\text{H}_2 \\
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow 2\text{CH}_3\text{CHOHCOOH}
\end{align*}
\]

One of the reasons that \(\text{H}_2\) yield decreases seems lactate production. Wang et al. reported that \(\text{H}_2\) yield decreases with the addition of acetate [10]. Zheng et al. also reported that \(\text{H}_2\) yield decreases with the addition of butyrate [11]. The metabolic shifts cause the decrease of \(\text{H}_2\) yield in this study. \(\text{H}_2\) partial pressure inhibits \(\text{H}_2\) productivity [12]. Mizuno et al. achieved a 68% increase of \(\text{H}_2\) yield by \(\text{N}_2\) sparging [13]. Kim et al. reported that \(\text{H}_2\) yield was improved from 0.77 mol mol-hexose\(^{-1}\) to 1.68 mol mol-hexose\(^{-1}\) by gas sparging of \(\text{N}_2\) and \(\text{CO}_2\), respectively [14]. Therefore continuous \(\text{H}_2\) production at short HRT with the decrease of \(\text{H}_2\) partial pressure would be future work to improve \(\text{H}_2\) productivity.

![Figure 2: The effect of HRT on \(\text{H}_2\) production rate and \(\text{H}_2\) yield.](image)

![Figure 3: The effect of HRT on VFA production rate.](image)

### 4 Conclusions

In this study, the following conclusions can be drawn:

- \(\text{H}_2\) 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.
- \(\text{H}_2\) 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.
References


