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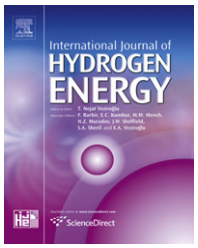

Effect of sludge recirculation on characteristics of hydrogen production in a two-stage hydrogen–methane fermentation process treating food wastes

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ABSTRACT

The two-stage hydrogen–methane fermentation process with different patterns of recirculation was investigated. Operations with the circulation of heat-treated sludge performed considerably better than those with the recirculation of raw sludge with respect to both the hydrogen production rate and yield. In addition, the results of the batch tests demonstrated that circulated sludge was capable of consuming hydrogen under acidogenic pH while the heat-treated sludge was not. These results suggest that the recirculation of active methanogenic sludge had an inhibitive effect on the hydrogen production, which can likely be attributed to the high hydrogen-consuming activity of microorganisms present in the circulated sludge. On the other hand, operations without any sludge recirculation did not perform well in terms of hydrogen production or carbohydrates degradation compared to those with recirculation, perhaps due to a shortage of available nitrogen. This suggests that sludge recirculation in effect supplemented the NH_4^+ in the hydrogen reactor.

1. Introduction

Bio-hydrogen production by anaerobic dark fermentation produces solvents, including organic acids and ethanol, which generally requires further treatment. A two-stage anaerobic dark fermentation process consisting of an acidogenic reactor producing hydrogen gas (a hydrogen reactor) and a methanogenic reactor producing methane gas (a methane reactor) is an effective system to consume such solvents with highly efficient energy recovery. Energy analysis performed by Ruggeri et al. suggested that the two-stage fermentation process had greater net energy recovery than the single hydrogen fermentation process [1]. Until now, the two-stage processes successfully produced hydrogen and methane from a variety of organic wastes, including food waste, water hyacinth, molasses, cassava stillage, and microalgal residues [2–6]. Although the two-stage fermentation process is present in the early stages of development, large-scale practical systems have been performed recently [7,8]. Over the past two decades, the characteristics of the hydrogen fermentation have been widely investigated. It is well known that hydrogen production is strongly affected by pH in a reactor, and the pH should be maintained in the 5.5–6.0 range [9–11]. To maintain appropriate pH levels, the addition of alkaline compounds such as NaOH or KOH is required [7,8,12]. In recent years, Chu [13], Lee [14] and Cavinato [15] have reported that a two-stage

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hydrogen-methane fermentation process with methanogenic sludge recirculation (two-stage recirculation process), with part of the methanogenic sludge circulated to a hydrogen reactor, was able to be successfully operated maintaining pH levels around 5.5 without any alkaline addition. Moreover, the process achieved stable hydrogen production with a 40–50% hydrogen concentration in biogas during the long-term continuous experiments treating food wastes. Cavinato [15] demonstrated that the circulated sludge could be substituted for alkaline compounds: In their experiment, the pH in the hydrogen reactor of the two-stage process without recirculation dropped below 4.3, and showed a very low level of hydrogen production meanwhile that of the other process with recirculation maintained appropriate pH around 5.4 [15]. Moreover, the two-stage recirculation process recorded 2.5–2.8 mol/mol-hexose of hydrogen yields [14,15], which were relatively large compared to the 4 mol/mol-hexose from the theoretical maximum hydrogen yield. As such, the two-stage recirculation process provides superior performance in hydrogen fermentation; however, it is still unclear whether the recirculation process is more efficient than the two-stage process with addition of NaOH for pH adjustment, and what effect the recirculation process has on the operation of the reactor besides the buffering ability.

The microbial community composition is an important factor affecting hydrogen yield in dark hydrogen fermentation using mixed microflora since the co-existence of hydrogen-producing bacteria and hydrogen-consuming microorganisms reduces the net hydrogen production in a hydrogen reactor. To avoid the presence of a hydrogen-consumer in a hydrogen reactor, the heat-treatment of seed sludge [16,17], low pH operation [18,19] and the addition of inhibiter [20] have been widely employed. Heat-treatment (70–100 °C, 15–120 min) is used to kill hydrogenotrophic methanogens present in seed sludge. Low pH and inhibiter addition is employed to inhibit growth of methanogens and to wash the out of the hydrogen reactor during operation. Considering these practices, it is clearly a basic policy in hydrogen fermentation processes using mixed cultures that the microbial community in a hydrogen reactor should be dominated by hydrogen-producing bacteria. However, a two-stage recirculation process seems to be against this basic policy because the recirculation of methanogenic sludge, which includes many of hydrogenotrophic methanogens and homoacetogens, likely results in the settling of hydrogen consumers in a hydrogen reactor regardless of their growth rates. This has the potential to decrease the hydrogen yield in a two-stage process. In reality, Cheng et al. reported that methanogen invasion in a hydrogen reactor had a negative effect on hydrogen production in a pilot study [8]. Considering what has been described above, there is still a need to explain in principal why the two-stage recirculation process achieved relatively large hydrogen yields in earlier studies.

The present study focuses on the effect of recirculation patterns on the characteristics of hydrogen fermentation in a two-stage recirculation process to improve our understanding of the differences between the two-stage processes with and without recirculation. Continuous operations of two-stage processes with different recirculation patterns and those without recirculation were investigated, and in all the experiments, the pH in the hydrogen reactor was controlled in the appropriate range around 5.5. The effects of presence of hydrogen consumers in the circulated sludge were evaluated by comparing the processes with recirculation of active methanogenic sludge and the processes with the recirculation of inactivated methanogenic sludge by heat-treatment. In addition, a comparison between processes with and without recirculation indicates that specific changes occur in a hydrogen fermenter because of recirculation.

2. Materials and methods

2.1. *Reactor set-up*

Fig. 1 illustrates the schematic diagrams of all the experimental processes investigated. The reactors used in this study were the same as those Lee [14] used in a previous study. The process consists of a thermophilic hydrogen reactor (55 °C) and a thermophilic methane reactor (55 °C). A feed tank storing substrate (4 °C) was mechanically stirred by impellers. The substrate was fed into a hydrogen reactor from the feed tank using a time-controlled roller pump (Furue Science: RP-LVS) twelve times a day. The hydrogen reactor used in all the experiments was a completely stirred tank reactor (CSTR) with impellers, with a working volume of 8 l. A methanogenic reactor was a baffled reactor consisting of three chambers, with a working volume of 40 l. The sludge in the methanogenic reactor was agitated by biogas circulation using an air pump (ULVAC, DAP-15). The temperature of the reactors was maintained at 55 °C by a water jacket. Operation of the process was divided into six periods with different recirculation patterns (phase 1–phase 6). In phase 1, methanogenic sludge was circulated from the last chamber of the methane reactor to the hydrogen reactor using a time-controlled roller pump (Furue Science: RP-LVS) twelve times a day. The flow rate of the recirculation was the same as that of feeding to the hydrogen reactor (Recirculation ratio: 1). The pH of the sludge was controlled above 5.3 by automatically dosing with 1 M NaOH solution (Mettler Toledo, pH transmitter 2050e). In phase 2, methanogenic sludge was circulated from the last chamber of the methane reactor to the hydrogen reactor. The pH of the sludge in the hydrogen reactor was controlled above 5.3 automatically by adding methanogenic sludge with a roller pump (Furue Science: RP-LVS), with a power supply controlled by a pH transmitter 2050e (Mettler Toledo). The recirculation ratio observed during operation in phase 2 was approximately 2.9. In phase 3, methanogenic sludge emitted from a methane reactor was inactivated by heat-treatment in an oven at 100 °C for an hour to kill methanogens and other bacteria present in methanogenic sludge. After that, the heated sludge was stored in the sludge storage tank illustrated in Fig. 1, and from there, the sludge was circulated to the hydrogen reactor. The pH in the hydrogen reactor was controlled above 5.3 automatically by the recirculation of sludge using the pH transmitter 2050e (Mettler Toledo). The recirculation ratio observed in phase 3 was approximately 2.9. In phase 4, methanogenic sludge stored in a sludge storage tank was circulated to the hydrogen reactor twelve times a day with a recirculation ratio 1. The pH in the hydrogen reactor was controlled above 5.3 by a 1 M