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Hydrogen and methane production from untreated rice straw and raw sewage sludge under thermophilic anaerobic conditions

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ABSTRACT

Bioenergy produced from co-digestion of sewage sludge (SS) and rice straw (RS) as raw materials, without pretreatment and additional nutrients, was compared for the one-stage system for producing methane (CH_4) and the two-stage system for combined production of hydrogen (H_2) and CH_4 in batch experiments under thermophilic conditions. In the first stage H_2 fermentation process using untreated RS with raw SS, we obtained a high H_2 yield (21 ml/g-VS) and stable H_2 content (60.9%). Direct utilization of post-H_2 fermentation residues readily produced biogas, and significantly enhanced the CH_4 yield (266 ml/g-VS) with stable CH_4 content (75–80%) during the second stage CH_4 fermentation process. Overall, volatile solids removal (60.4%) and total bioenergy yield (8804 J/g-VS) for the two-stage system were 37.9% and 59.6% higher, respectively, than the one-stage system. The efficient production of bioenergy is believed to be due to a synergistically improved second stage process exploiting the well-digested post-H_2 generation residues over the one-stage system.

1. Introduction

Anaerobic digestion has been traditionally used as an effective and economical technology for the biological treatment of organic wastes. It contributes not only to high treatment efficiency but also biogas (methane (CH_4)) producing ability [1]. Sewage sludge (SS), in the form of a nitrogen-rich organic fraction after biological wastewater treatment process, exhibits higher energy potential, and biodegradability. Therefore, SS has been widely used for biogas production, generating sustainable bioenergy [2,3]. On the other hand, lower biogas yields via anaerobic digestion are observed when low solid content in SS ranges between 0.8% and 9% [3,4]. In addition, SS has a low carbon to nitrogen (C/N) ratio of about 7 [5]. It has been reported that a proper C/N ratio for anaerobic digestion is in the range of 20–30 [6]. Therefore, the efficient

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utilization of SS for enhanced biogas production will require admixing with another type of carbon-rich organic waste. A literature survey revealed that rice straw (RS), a dry agriculture residual, is a rich source of carbon with a C/N ratio of more than 40 [5,7]. To obtain a highly economical and efficient biogas production from the RS, supplementation of nitrogen sources, such as SS and domestic animal waste is typically required [7]. The RS is also a lignocellulosic material, mainly consisting of lignin, cellulose, and hemicelluloses; cellulose and hemicelluloses as the carbohydrates are converted into biogas via anaerobic digestion [8]. To improve anaerobic digestion performance, these organic wastes, i.e., SS and RS require a pretreatment step employing some sort of heat or chemical treatment prior to fermentation in order to disrupt the microbial cells in SS [2]. Zhu et al. [9] reported that high hydrogen (H_2) and CH_4 production in the two-stage system obtained from co-substrate of SS and food waste by heat treatment in comparison to without any treatment. These treatments also help remove lignin and release carbohydrates from the barely degradable RS [7,8,10]. Siddiqui et al. [11] demonstrated that the proper admixture of SS and food waste improved H_2 and CH_4 production in the two-stage reactors under controlled pH conditions during the fermentation process. However, these pretreatment methods and controlling the pH require a high-energy input, large quantities of chemical, and a sizable expenditure, which prohibits the implementation of a practical fermentative bioenergy production technology. Besides that, the above H_2 production cases [11,12] have been investigated under liquid anaerobic digestion as for total solids (TS) concentration between 0.5% and 10%. Solid-state anaerobic digestion (TS $>$ 15%) has processing and technical advantages over the liquid anaerobic digestion currently used for producing biogas [6]. To date, general guidelines such as TS concentration of 10% or more, especially first stage H_2 fermentation process in the two-stage system, have not been sufficiently provided as yet. As the technologies for commercializing H_2 and CH_4 production have not yet been clearly defined, we believe that there is a clear need for new basic research on utilization of organic wastes as such (i.e., without pretreatment steps and pH control), while still maintaining high yields of H_2 and CH_4.

Recently, biological H_2 production has emerged as an important byproduct from the co-digestion of SS infused with a certain amount of RS due to the balanced C/N ratio in batch experiments [13]. In addition, the two-stage process has been found to simultaneously promote energy conversion efficiency, organic solids removal, and CH_4 production at a rate more than that obtained with a one-stage CH_4 production process, especially under thermophilic conditions [14,2]. Fezzani and Ben Cheikh [15] demonstrated that CH_4 production in second reactor could be enhanced by acidified olive mill wastes as a co-substrate from first reactor for the acidification process. Therefore, looking at the dual use potential of SS and RS in the production of H_2 and CH_4, it may be promising to exploit the two-stage anaerobic digestion process technology to this end. To the best of our knowledge, anaerobic co-digestion of the SS with RS using the two-stage H_2 and CH_4 production process has not been reported.

Based on these requirements, we assessed the sequential production of H_2 and CH_4 following co-digestion of raw SS and untreated RS, without additional nutrients and pH control, in a two-stage H_2 and CH_4 fermentation process, under thermophilic conditions. The study has two objectives: first, to propose a simple and cost-effective H_2 fermentation process as the first stage, without pretreatment of feedstock/inoculum under solid-stage conditions, i.e., direct mixing of RS and SS, to give high yields of H_2, and second, to discuss the efficient and direct use of residues from the first stage for CH_4 production. In addition, we also examined the feasibility of biogas production compared to the one-stage CH_4 fermentation process using a mixture of either SS and RS, or SS and RS alone; i.e., the total bioenergy yields from one- or two-stage processes were estimated. To the best of our knowledge, the present study is the first report on H_2 production under high solid-state conditions, and the direct use of post-H_2 generation residues for subsequent CH_4 fermentation from both organic wastes without any pretreatment in order to reduce energy input and achieve cost-effective H_2/CH_4 production in the two-stage system.

2. Materials and methods

2.1. *Feedstock and inocula*

Sewage sludge (SS) used as inocula or feedstock in this study was obtained from a gravity sludge thickener line in the wastewater treatment plant from Kasumigaura sewer office (Ibaraki prefecture, Japan). The SS was filtered through a 2 mm sieve to remove coarse particles, and then stored at 4 °C. The volatile suspended solids (VSS), alkalinity as $CaCO_3$, and pH of the SS were 7.4 g/l, 4.8 g/l and 6.4, respectively. For the two-stage process, microorganisms (especially naturally occurring bacteria) in SS served as an inoculum for H_2 production as first-stage (hydrolytic–acidogenic step). The SS, as substrate/inoculum, was acclimated by self-fermentation in a batch reactor under thermophilic anaerobic conditions at 55 °C for one month. The acclimated sludge, which produced biogas with over 80.0% CH_4 content, was used as the next inoculum source for CH_4 production at second stage (methanogenic step). The RS, obtained from a local farmer (Chiba prefecture, Japan), was used as untreated feedstock. The RS was chopped and milled to a particle size of approximately under 2 mm, and then stored in a plastic bag at room temperature. The main composition of RS on a dry weight basis was as follows: 81.4% of volatile solids (VS), and 17.8% of lignin. The characteristics of SS and RS are described in Table 1.

2.2. *Experimental design*

Table 2 summarizes the operational conditions of one- or two-stage anaerobic digestion process. The total volume of 500-ml anaerobic bottle (SIBATA, Tokyo, Japan) was employed as batch fermentation reactor. The concentration of total solids (TS) and volatile solids (VS) was calculated as follows:

$$TS = \frac{\{(R \times C_0) + (S \times C_0)\}}{V} \times 100 \quad (1)$$

where TS (%) is the TS concentration; *R* (g) is the mass of RS; *S* (ml) is the mass of SS; C_0 is the concentration of TS from RS and SS; *V* (ml) is the working volume.