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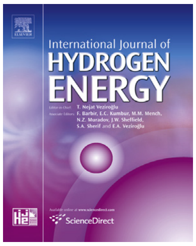

Simultaneous coproduction of hydrogen and methane from sugary wastewater by an "$ACSTR_H–UASB_{Met}$" system

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ABSTRACT

A two-phase "$ACSTR_H–UASB_{Met}$" system has been investigated at the stepwise decreased HRT for the simultaneous production of hydrogen and methane in this study. Hydrogen could be continuously produced from the two-phase hydrogen fermentation of sugary wastewater in ACSTR and effluents from hydrogen fermentation were converted into methane in UASB reactor. At optimum conditions (HRT_H: 5 h, HRT_{Met}: 15 h), the highest hydrogen production rate of 5.69 (±0.06) mmol L^{-1} h^{-1} was obtained from sugary wastewater and methane was continuously produced from effluents of hydrogen fermentation with a production rate of 3.74 (±0.13) mmol L^{-1} h^{-1}. The total bioenergy recovery by coproduction of hydrogen and methane from sugary wastewater reached 19.37 W and a total of 92.41% of substrate was converted to the biogas (hydrogen and methane) with two-phase anaerobic fermentation.

1. Introduction

The current imperative global issues such as petroleum depletion and global warming are leading to new developments in the fuel markets all over the world. Bioenergy like hydrogen and methane have the potential to replace a part of our need for fossil fuels, especially in the transport sector because of their assumed many merits and perceived environmental benefits [1]. Among many bioenergy production methods, a great deal of attention has been focused on anaerobic production of hydrogen rather than methane in particular because it has many advantages including no carbon dioxide emission and high energy density [2–6]. The exploration of substrate for hydrogen production is a vital and effective way of tapping clean energy from renewable sources in a sustainable approach. The main substrate for fermentative hydrogen production was synthetic wastewater containing carbohydrates substances. Numerous studies have been focused on glucose and sucrose and optimal operation parameters such as hydraulic retention time (HRT), organic loading rate (OLR), pH and temperature were fully investigated [7,8]. While in terms of the dual benefit of fermentative hydrogen production and waste degradation, carbohydrate-rich actual wastewaters were often utilized as substrates.

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Cheese whey wastewater [9], rice winery [10], and apple processing wastewater [11] were proved to be feasible substrates showing the maximum hydrogen production rate of 2.79, 7.09, 4.02 mmol L^{-1} h^{-1}, respectively. To improve energy recovery, the two-phase anaerobic fermentation process for coproduction of hydrogen and methane has attracted a great deal of attention. Until now this process has been operated with various types of actual wastes including food waste [12], olive pulp [13] and red canary grass [14]. However, to the best of our knowledge, there is no paper on the utilization of sugary wastewater as a sole carbon source for sequential coproduction of hydrogen and methane from a two-phase process.

Hydrogen production by anaerobic fermentation process is highly dependent on the conditions of this process, such as pH, OLR, HRT and hydrogen partial pressure, which affect the microbial metabolic balance and subsequent fermentation metabolites. Among these conditions, as HRT is related to the amount of organics that can be handled per unit time [15], it has a direct impact on substrate uptake efficiency, microbial population and metabolic pathway. It is generally held that high HRT allows for growth, by not washing out slow growing methanogens and acetogens, including competitors for substrates. However, a low HRT may reduce substrate uptake efficiency, active biomass retention, and therefore, the overall process efficiency [16]. Based on above information, this study aimed to investigate the fermentative bioproduction of hydrogen from sugary wastewater in anaerobic continuous tank stirred reactor (ACSTR) at various HRT. The effluents of fermentative hydrogen production process were used for continuous methane production in an upflow anaerobic sludge bed (UASB) at various HRT, the total bioenergy recovery of hydrogen and methane coproduction from sugary wastewater was evaluated.

2. Material and methods

2.1. *Substrate and inoculums*

In this study, the sugar wastewater used as experimental substrate for sequential hydrogen and methane coproduction was collected from local sugar refining industry (Harbin, China). As shown in Table 1, the sugary wastewater contained a high concentration of carbohydrates which correspond to readily fermentative sugars. In addition, it contained enough nitrogen and phosphorus sources which are essential for cultivation of microorganisms. On one hand, diluted sugary wastewater with COD concentration of 6 g L^{-1} was used as substrate for the first-phase acidogenic reactor. On the other hand, the effluent of the acidogenic reactor was used as substrate (pH was adjusted to about 7.0 with alkali addition) for the second-phase methanogenic reactor.

Table 1 – The characteristics of sugar wastewater used in this study.

Parameters	Values[a]	Parameters	Values[a]
Total suspend solid (TSS)	3.3 g L^{-1}	Alkalinity	1.1 g L^{-1}
Volatile suspended solid (VSS)	1.5 g L^{-1}	Total nitrogen (TN)	2.2 g L^{-1}
Total chemical oxygen demand (TCOD)	27.3 g L^{-1}	SO_4^{2-}	1.3 g L^{-1}
Chemical oxygen demand (COD)	26.7 g L^{-1}	PO_4^{3-}	0.41 g L^{-1}
Total organic carbon (TOC)	11.6 g L^{-1}	pH	6.5
Carbohydrates	9.8 g L^{-1}		

a Values were averaged of 5 determinations.

The raw sludge was obtained from a local municipal wastewater treatment plant (Harbin, China) and screened by a sieve. To be used as inoculum for hydrogen production, the raw sludge was inoculated into the sequencing batch reactor (SBR) with sugary wastewater and enriched by aerating intermittently to inactivate hydrogen-consuming bacteria, especially methanogens. The system pH was controlled at 4.5 (±0.2) using alkali solution. During the enrichment process, biological activity of hydrogen-producing bacteria was examined by analyses of glucose consumed. After enough enrichment over 30 days, the hydrogenic sludge with TSS 12.91 (±0.43) g L^{-1} and VSS 8.35 (±0.12) g L^{-1} was inoculated within the acidogenic reactor of the two-phase anaerobic fermentation process. In case of methane production, without any pretreatment, the raw sludge with TSS 21.54 (±0.17) g L^{-1} and VSS 14.22 (±0.26) g L^{-1} was inoculated into the methanogenic reactor of the two-phase anaerobic fermentation process. The system pH was controlled at 6.9 (±0.2) which is susceptible for the effective function of methanogenic metabolic process. Operating temperature for the reactor with sugary wastewater was 35 °C. Metabolism activities of methanogens were examined by detecting methane content in produced biogas from methanogenic reactor. After the methanogenic sludge got enough enrichment over three months, the effluent of the acidogenic reactor began to be used as the substrate for methanogenic reactor with addition of alkali solution to regulate pH.

2.2. *Integrated two-phase fermentation system*

An integrated two-phase "$ACSTR_H$–$UASB_{Met}$" anaerobic fermentation system was designed for simultaneous hydrogen and methane production in this study. The system consisted of acidogenic reactor for hydrogen production and a methanogenic reactor for methane production. The acidogenic reactor was anaerobic continuous stirred tank reactor (ACSTR). It had a working volume of approximately 7 L with an internal diameter of 18.5 cm and a height of 26 cm, and was operated in a continuous flow mode and mixed completely by a variable speed gear shaft mixer. After the enriched hydrogenic sludge was inoculated into this acidogenic reactor, a rest of the volume in the reactor was filled with the sugary wastewater under complete anaerobic condition with the aid of peristaltic pump. The system temperature was constantly maintained at 35 °C by an electric jacket. The acidogenic reactor was operated in a continuous mode by supplying the sugary wastewater continuously at decreased HRT in steps. Five levels of HRT were designed to 12, 8, 6, 5 and 4 h, respectively.

The upflow anaerobic sludge blanket reactor (UASB) was used as the methanogenic reactor. It was also operated in a continuous mode at decreased HRT: 35, 27, 21, 15 and 10 h,