Bioresource Technology 198 (2015) 198–206

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Bio-hydrogen and bio-methane potentials of skim latex serum in batch thermophilic two-stage anaerobic digestion

Rattana Jariyaboon [a,b,*], Sompong O-Thong [c,d], Prawit Kongjan [a,b]

[a] Chemistry Division, Department of Science, Faculty of Science and Technology, Prince of Songkla University (PSU), Pattani 94000, Thailand
[b] Bio-Mass Conversion to Energy and Chemicals (Bio-MEC) Research Unit, Faculty of Science and Technology, Prince of Songkla University (PSU), Pattani 94000, Thailand
[c] Department of Biology, Faculty of Science, Thaksin University (TSU), Phathalung 93110, Thailand
[d] Microbial Resource and Management (MRM) Research Unit, Department of Biology, Faculty of Science, Thaksin University (TSU), Phathalung 93110, Thailand

HIGHLIGHTS

- First report on bio-hydrogen and bio-methane potentials of skim latex serum (SLS).
- The bio-hydrogen potential of 1.57 L/L SLS was obtained.
- The bio-methane potential of 12.2 L/L SLS was also generated.
- The maximum energy production from SLS was 12 kJ/g VS.
- Two-stage anaerobic digestion could efficiently remove organic content from SLS.

ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form 2 September 2015
Accepted 5 September 2015
Available online 10 September 2015

Keywords:
Bio-hydrogen potential
Bio-methane potential
Skim latex serum
Two-stage anaerobic process

ABSTRACT

Anaerobic digestion by two-stage process, containing hydrogen-producing (acidogenic) first stage and methanogenic second stage, has been proposed to degrade substrates which are difficult to be treated by single stage anaerobic digestion process. This research was aimed to evaluate the bio-hydrogen and the bio-methane potentials (BHP and BMP) of skim latex serum (SLS) by using sequential batch hydrogen and methane cultivations at thermophilic conditions (55 °C) and with initial SLS concentrations of 37.5–75.0% (v/v). The maximal 1.57 L H_2/L SLS for BHP and 12.2 L CH_4/L SLS for BMP were both achieved with 60% (v/v) SLS. The dominant hydrogen-producing bacteria in the H_2 batch reactor were *Thermoanaerobacterium* sp. and *Clostrdium* sp. Meanwhile, the CH_4 batch reactor was dominated by the methanogens *Methanosarcina mazei* and *Methanothermobacter defluvii*. The results demonstrate that SLS can be degraded by conversion to form hydrogen and methane, waste treatment and bioenergy production are thus combined.

1. Introduction

Thailand is the global leader in natural rubber production. According to a report from the Rubber Research Institute, Thailand (www.rubberthai.com), among the annual approximately 3.7 million tons of rubber products, concentrated latex produced by centrifugation ammoniated field latex contributes about 20%. Additionally, the Department of Industrial Works, Ministry of Industry of Thailand, reported there are 61 concentrated latex factories currently operated in Thailand. Meanwhile, concentrated latex processing generates large amount of high strength and sulfate rich wastewater. For producing 0.4 ton of concentrated latex from 1 ton of ammoniated field latex, approximately, 2.4 m^3-mixed wastewater majorly comprising of wash water and skim latex serum (SLS) discharged from centrifugation of ammoniated field latex and sulfuric acid coagulation of skim latex, respectively. Thus, wash water contains large amount of ammonia, whereas SLS is the main sources of organic matters, sulfate, and ammonia (Jawjit and Liengcharernsit, 2013). Mixed wastewater from concentrated latex processing has been widely treated via the series of facultative/anaerobic pond and aerated lagoon/activated sludge. Nonetheless, this kind of open treatment system could consequently emit methane, one of major greenhouse gases and hydrogen sulfide having foul odor of rotten eggs into the atmosphere. Methane and hydrogen sulfide are typically formed by anaerobic

* Corresponding author at: Chemistry Division, Department of Science, Faculty of Science and Technology, Prince of Songkla University (PSU), Pattani 94000, Thailand. Tel.: +66 73 313928 50x1845, mobile: +66 808721260.
E-mail address: rattana.sa@psu.ac.th (R. Jariyaboon).

http://dx.doi.org/10.1016/j.biortech.2015.09.006
0960-8524/

digestion of organic matters and sulfate, respectively. Since about 0.58 m^3 of SLS produced per 1 ton of field latex, the amount of SLS is about 1.5 times that of concentrated latex produced. Thus, roughly a million tons of SLS is annually generated in Thailand, making it a significant waste stream (Phoolphundh et al., 2013). To overcome serious air pollution caused by treating mixed wastewater in open anaerobic system, SLS should therefore be treated separately through a close anaerobic digestion system for recovering gaseous bio-fuel in a form of biogas due to its high content of organic matters of proteins, carbohydrates, and lipids. However, during the traditional anaerobic digestion of sulfate rich SLS, sulfate reducing bacteria (SRB) could generate significant amount of sulfide, which is directly inhibit to methanogens at even low concentration as 0.002–0.003 M (Boe, 2006) and consequently leading to process failure.

The division of the anaerobic digestion into two stages of acidogenesis and methanogenesis could potentially reduce the sulfate concentration in the first stage. H_2S can be then removed before the methanogenesis in the second stage. This improves the digestion efficiency relative to a single stage process (Phoolphundh et al., 2013; Jawjit and Liengcharernsit, 2013; Kongjan et al., 2014). Furthermore, evidence suggests that two-stage anaerobic digestion has a better reaction extent than single stage, leaving less undigested waste and providing more methane for better economics (Demirel et al., 2010). Moreover, from an anaerobic two-stage process of various carbohydrates rich substrates also a mixture of hydrogen and methane, known as bio-hythane could possibly be recovered (Kongjan et al., 2013). Such bio-hythane is a renewable clean energy source, which is more powerful and stable combustion, and less releasing greenhouse gases than single biogas/natural gas in internal combustion engines (Alavandi and Agrawal, 2008; Porpatham et al., 2007).

In a two-stage anaerobic process, wastewater is anaerobically digested sequentially in two separate bioreactors. Each stage should be operated with near optimal pH, hydraulic retention time (HRT), and nutrient concentration, to accomplish effective fermentation. The pH range 5–6 is suitable in the first reactor for both acidogenic (hydrogen producing) bacteria and sulfate reducing bacteria. In this step, SRB reduce sulfate to sulfide, meanwhile acidogens convert carbohydrates to hydrogen via the acetate and butyrate pathways, while other volatile fatty acids and solvents are simultaneous produced (Han and Shin, 2004; Hwang et al., 2009). However, this hydrogen producing stage removes only 10–20% of the organic matter in volatile solids (VS). Thus, the first stage effluent must be further treated in a second stage, which has an optimal pH range of 7–8, and here methane is produced by methanogens (Kongjan et al., 2013). There are cases reported where anaerobic fermenting at a moderate thermophilic temperature (50–65 °C) provided higher hydrogen and methane yields than mesophilic conditions (25–40 °C). This is because increasing cultivation temperature, increases chemical and biological reaction rates (Kargi et al., 2012).

Two-stage anaerobic digestion is an increasingly popular method for simultaneous treating organic wastes and recovering energy carrier in a form of bio-hythane. Thus, the bio-hydrogen and bio-methane potentials (BHP and BMP) as a simulated two-stage process for hydrogen production and followed by methane production are necessary to be investigated as the indicator of the ultimate anaerobic biodegradability of a substrate (Giordano et al., 2011). They are also necessary for assessing design, economic and managing issues of full scale implementations using anaerobic digestion (Angelidaki and Sanders, 2004). There are only few prior published studies on two-stage anaerobic digestion of waste water from concentrated latex industry (Phoolphundh et al., 2013; Jawjit and Liengcharernsit, 2013), and SLS for the BHP and followed by BMP has not been investigated. This study characterized SLS in terms of its BHP and BMP in thermophilic two-stage anaerobic digestion, varying the SLS concentration for near optimal biodegradability.

2. Methods

2.1. Skim latex serum (SLS)

Fresh raw SLS was collected from an acid coagulation pond of Chana Latex Co, Ltd., Songkhla, Thailand. The pH of the yellowish raw SLS was 4.97 ± 0.01. The collected SLS was stored at 4 °C until use, in order to minimize self-biodegradation and acidification.

2.2. Inoculums for first stage anaerobic digestion (hydrogen production)

The inoculums for hydrogen production were collected from two different sources. Anaerobically digested sludge was collected from the biogas production system of Chalong Latex Industry CO., Ltd., Songkha, Thailand, and was used as original mesophilic seeds. Thermophilic anaerobic digested sludge was received from the first tank of the thermophilic two-stage anaerobic digestion system, using palm oil mill effluent as substrate, of the Faculty of Science, Thaksin University, Thailand.

Unlike for methane production in the second stage of anaerobic digestion, for the first stage the seed sludge must be pretreated to enrich hydrogen-producing bacteria and to inactivate hydrogen-consuming bacteria. Effects of the two inoculums (mesophilic and thermophilic) and different pretreatment methods (load-shock and heat-shock pretreatment) on hydrogen production were investigated.

In the heat-shock treatment the sludge was held at 100 °C for 30 min in an autoclave prior to use in cultivation (O-Thong et al., 2009). In the load-shock treatment glucose was added to the broth to obtain the high 50 g/L glucose loading at the beginning of fermentation (Kongjan et al., 2011).

To select the best inoculums for hydrogen stage, batch cultivation was conducted in 500 mL bottles with 200 mL working volume of the mixture, 50 mL inoculums, 75 mL SLS, and 75 mL basic anaerobic (BA) medium (supplementing with 10 g/L glucose), corresponding to initial substrate concentration of 18 g VS/L. The composition of the BA medium has been reported elsewhere (Angelidaki and Sanders, 2004). The mixtures were then purged with 1 L/min of nitrogen gas for 3 min to ensure anaerobic conditions, and the bottles were closed with butyl stoppers and placed in a 55 °C – incubator for 3 days.

2.3. Bio-hydrogen potential (BHP) determination

The first stage anaerobic biodegradability of SLS was tested at various SLS concentrations by using inoculum selected from Section 2.2. Also a pure culture of *Thermoanaerobacterium* strain 112YL was used as inoculum in SLS fermentation. The batches used a 200 mL working volume in each 500 mL serum bottle. The culture consisted of 25% v/v of thermophilic inoculum, 37.5–75.0% v/v of SLS, with the rest being BA medium (without addition of glucose). The substrate was cultivated at 55 °C. The headspace gas was collected for hydrogen determination every 12 h.

2.4. Bio-methane potential (BMP) determination

The thermophilic inoculum for methane production stage was obtained from the second tank of the thermophilic two-stage anaerobic digestion system, using palm oil mill effluent as substrate, of the Faculty of Science, Thaksin University, Thailand.