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Hydrogen and methane production in extreme thermophilic conditions in two-stage (upflow anaerobic sludge bed) UASB reactor system

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ABSTRACT

Two-stage hydrogen and methane production in extreme thermophilic (70 °C) conditions was demonstrated for the first time in UASB-reactor system. Inoculum used in hydrogen and methane reactors was granular sludge from mesophilic internal circulation reactor and was first acclimated for extreme thermophilic conditions. In hydrogen reactor, operated with hydraulic retention time (HRT) of 5 h and organic loading rate (OLR) of 25.1 kg COD/m^3/d, hydrogen yield was 0.73 mol/mol $glucose_{added}$. Methane was produced in second stage from hydrogen reactor effluent. In methane reactor operated with HRT of 13 h and OLR of 7.8 kg COD/m^3/d, methane yield was 117.5 ml/g COD_{added}. These results prove that hydrogen and methane can be produced in extreme thermophilic temperatures, but as batch experiments confirmed, for methane production lower temperature would be more efficient.

1. Introduction

Hydrogen is a valuable and versatile fuel that can be utilized in many purposes such as traffic, heat and power production. Nowadays most of the hydrogen is produced in steam reforming process, which is very energy intensive and not sustainable [1]. For this reason further research is directed to other more environmentally friendly hydrogen production methods. One of the promising techniques is dark fermentation, where anaerobic bacteria can utilize organic wastes to produce hydrogen. The challenge of this process is that H_2 production is accompanied by the production of soluble end products such as volatile fatty acids (VFAs) and alcohols and additional step for chemical oxygen demand (COD) removal is needed [2]. On the other hand organic acids and alcohols are suitable substrates for methane production [3]. Therefore two stage combined hydrogen and methane production process could offer an efficient solution. First stage is optimized for hydrogen production and second stage for methane production by adjusting process parameters, such as pH and hydraulic retention time (HRT). By separating these two phases can offer several advantages compared to single stage process. With particulate substrates hydrolysis and acidification are improved as they are controlled in first stage in separate reactor [4]. This also increases the stability of the process. In addition the energy recovery is maximized since hydrogen is recovered and methane production is improved [4,5].

Hydrogen can be produced in wide temperature range from psychrophilic (<25 °C) to extreme thermophilic conditions (>70 °C) [6–8]. Usually higher temperatures are preferred and especially extreme thermophilic conditions seem to offer several advantages. It has been confirmed that due to better

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thermodynamics and higher rate of hydrolysis in extreme thermophilic (≤70 °C) conditions hydrogen yields can reach close to theoretical maximum (4 mol/mol glucose) [9–12]. High temperature also offers better pathogen removal, which is important especially when treating waste materials [13]. Methane production has also proved to be possible in extreme thermophilic condition, but for methane production higher temperatures may lead process instability and especially in extreme temperatures yields have been low [14–17]. However some industrial processes especially in pulp and paper industry produce hot and concentrated process water streams, which in economical point of view would be feasible to treat without cooling especially if the water is circulated back to the process.

Upflow anaerobic sludge bed (UASB) reactors and its modifications such as internal circulation (IC) and expanded granular sludge bed (EGSB) reactors have been used widely to anaerobic treatment of industrial wastewaters and to produce methane. Also hydrogen production in UASB reactor system has gained interest, as it seems to be more stable than other reactor systems [18]. The main feature of the UASB reactor is the formation of anaerobic granules [19]. The granules have high settling properties, which leads to good biomass retention and allows high loading with short HRT, also in thermophilic conditions [20].

In this paper two-stage hydrogen and methane production was studied in extreme thermophilic conditions, by using UASB reactors. Also batch experiments were conducted to compare methanogenic activity of the sludge grown in extreme thermophilic UASB at 70 and 55 °C.

2. Materials and methods

2.1. Reactor setup

The two-stage process consisted of two UASB-reactors for hydrogen and methane production with volumes of 200 ml (diameter 3.2 cm, height 28.8 cm) and 500 ml diameter 4.7 cm, height 36.2 cm respectively (Fig. 1). Feed was continuously pumped (Masterflex) into hydrogen reactor from two different feed containers for glucose and BA-media separately. Feed was kept at 4 °C. Effluent from hydrogen reactor was collected daily in the container at room temperature. Then, sodium bicarbonate buffer (5 g/l) was added, and the effluent was used as feed for methane reactor. Both UASB reactors were kept at 70 °C by circulating hot water in rubber hose surrounding reactors. HRT and OLR were 5 h and 25.1 kg COD/m^3/d, and 13 h and 7.8 kg COD/m^3/d for hydrogen and methane reactor, respectively.

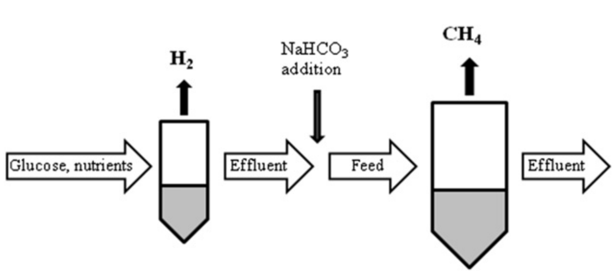

Fig. 1 – Schematic diagram of two stage UASB reactor system used to produce hydrogen and methane at 70 °C.

2.2. Substrate and inoculum

Granular sludge from mesophilic IC reactor treating vegetable processing wastewater (Lännen tehtaat Oyj, Säkylä, Finland) was used as inoculum for both hydrogen and methane reactors. Inoculum was first acclimated for extreme thermophilic conditions, by running reactors for 30 days at 70 °C with process parameters stated in Section 2.1. Then reactors were stopped. Meanwhile inoculum was stored at 4 °C in anaerobic conditions to minimise microbial decay and loss of microbial activity. For actual run 140 ml and 350 ml of adapted granular sludge were added to hydrogen and methane reactor, respectively.

The feed of hydrogen reactor consisted of glucose solution (5 g/l) and BA-media. BA-media was prepared according to [21] without resazurin and $NaHCO_3$.

2.3. Batch experiment

Set of batch assays were conducted to assess the methanogenic activity of the 70 °C methane reactor sludge at both 70 °C and at 55 °C. Batch assays were carried in triplicates in 120 ml serum vials with liquid volume of 60 ml. Each vial contained 15 g_{ww} of sludge from 70 °C methane reactor and 45 ml of effluent from hydrogen reactor. Sodium bicarbonate ($NaHCO_3$) buffer (5 g/l) was added to each vial. Sludge and effluent for the assays were collected at the end of reactor experiment on day 73. Vials were closed with butyl rubber stoppers and sealed with aluminium caps. Headspace of each vial was flushed with nitrogen gas to assure anaerobic conditions. Assays were conducted at 55 and 70 °C and gas volumes were corrected to standard temperature (0 °C) and pressure (760 mm Hg).

2.4. Analysis

Gas composition (CH_4, H_2 and CO_2) was analyzed with a Perkin Elmer Arnel Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD) and a Supelco Carboxen™ 1010 PLOT fused silica capillary column (30 m * 0.53 mm). Argon (15 ml/min) was used as the carrier gas and the temperatures of the oven, detector and injector were 200, 230 and 225 °C, respectively. The pH was measured with a Mettler Toledo Seven Easy pH meter. VFAs and alcohols were analyzed with a Perkin Elmer Autosystem XL gas chromatograph equipped with a flame-ionization detector (FID) and a HP-INNOWax column (30 m × 0.32 mm × 0.25 μm). Helium was used as a carrier gas and the temperature of the oven, detector and injector were 100–160, 225 and 230 °C respectively. Glucose was analyzed with phenol–sulphuric acid method according to [22]. COD was analyzed according to SFS 5504 [23].

3. Results and discussion

3.1. Inoculum acclimation

Mesophilic granular sludge was first acclimated for extreme thermophilic conditions running the two stage reactor system for 30 days at 70 °C. During acclimation period hydrogen production started immediately and on fifth day of operation