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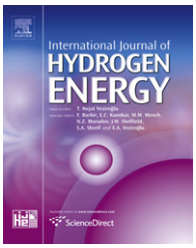

Hydrogen production using sono-biohydrogenator

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ABSTRACT

Hydrogen production in a novel sonicated biological hydrogen reactor (SBHR) was investigated and compared with a continuous stirred tank reactor (CSTR). The two systems were operated at a hydraulic retention time (HRT) of 12 h and two organic loading rates (OLRs) of 21.4 and 32.1 g COD/L.d. The average hydrogen production rates per unit reactor volume for the conventional CSTR were 2.6 and 2.8 L/L.d, as compared with 4.8 and 5.6 L/L.d for SBHR, at the two OLRs, respectively. Hydrogen yields of 1.2 and 1.0 mol H_2/mol glucose were observed for the CSTR, respectively, while for the SBHR, the hydrogen yields were 2.1 and 1.9 mol H_2/mol glucose at the two OLRs, respectively. The hydrogen content in the SBHR's headspace was higher than that in CSTR by 10% and 31% at OLRs of 21.4 and 32.1 g COD/L.d, respectively. Both glucose conversion efficiency and HAc/HBu ratio in the SBHR were higher than in the conventional CSTR at both OLRs. The biomass yield of about 0.32 g VSS/g COD observed in the CSTR and 0.23 g VSS/g COD in the SBHR substantiate the higher H_2 yield in the SBHR. DGGE analysis confirmed the specificity of the microbial hydrogen-producing culture in the SBHR, with two different hydrogen producers (*Clostridium* sp. and *Citrobacter freundii*) detected in the SBHR and not detected in the CSTR.

1. Introduction

Hydrogen, as an energy carrier, offers numerous advantages over other conventional energy carriers. Hydrogen combustion provides energy based on mass basis with lower heating value (LHV), which is 2.4, 2.8, and 4 times higher than methane, gasoline and coal respectively [1]. In addition, hydrogen gas has the potential to be a useful energy carrier in a wide range of applications through the use of fuel cells, and is expected to become more important in the future [2,3]. The major advantage of energy from hydrogen is the absence of polluting emissions since the utilization of hydrogen, either via combustion or via fuel cells, results in pure water [4].

At present, hydrogen is produced mainly from fossil fuels, biomass, and water using chemical or biological processes. Anaerobic (or dark) fermentation and photosynthetic degradation are the two most widely studied biohydrogen production techniques [5]. Anaerobic fermentation is promising for sustainable hydrogen production since organic matter, including waste products, can be used as a feedstock for the process [6]. However, the rate of biological H_2 production is low and the technology needs further development [7]. Current H_2 yields reported in the literature are usually in the range of 1–2 mol H_2/mol glucose converted [8], much less than the theoretical maximum of 4 mol H_2/mol glucose converted. Therefore, improving the H_2 yield from dark fermentation of organics is an active area of research [9].

Hydrogen partial pressure and the resulting H_2 concentration in the liquid phase are key factors affecting fermentative H_2 production [10]. Generally, high H_2 partial pressure has a negative effect on H_2 production by decreasing the activity of *hydrogenase* and making the H_2 production reaction thermodynamically unfavourable [11]. Various techniques have been used to remove metabolic gases (H_2, CO_2) from the

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liquid phase [12]. Gas sparging has been the most common method used to decrease the concentrations dissolved gases in fermentative H_2-producing reactors. Various gases have been used to decrease the dissolved hydrogen concentration in the liquid such as nitrogen [13,17], CO_2, methane [18], biogas [16], argon [19], argon and H_2 sparging [20]. Other techniques to decrease concentrations of dissolved gases include increased stirring [21], decreasing the reactor headspace pressure i.e. applying a vacuum [10], and using an immersed membrane to directly remove dissolved gases [22]. Table 1 summarizes some studies which used gas sparging to enhance the hydrogen production. As shown in the table, the maximum increases in hydrogen yield were 66%, 88% and 118% using the N_2, CO_2, and methane, respectively.

Ultrasonication causes a localised pressure drop to below the evaporating pressure in the aqueous phase, resulting in the formation of micro bubbles or cavitation bubbles [23]. During cavitation, micro bubbles form at various nucleation sites in the fluid and grow during the rarefaction phase of the sound wave [24]. Subsequently, in the compression phase, the bubbles implode and the collapsing bubbles release a violent shock wave that propagates through the medium [25].

Based on an extensive search, there are only a limited number of studies (six studies) where the impact of ultrasonication on biological hydrogen production has been investigated. Table 2 summarizes the six studies which applied ultrasonication either on substrate or on the seed to enhance hydrogen production. Three studies applied ultrasonication on sewage sludge as a substrate [26–28], and the other three applied the ultrasonication on the seed biomass [29–31]. Guo et al. [29] studied the impact of ultrasonic pre-treatment on hydrogen production from boiled anaerobically digested sludge at 90 °C for 15 min with sucrose as substrate. In another study, More and Ghangrekar [30] evaluated the effect of ultrasonication pre-treatment on mixed anaerobic sludge to inoculate the microbial fuel cells, and reported that the ultrasonication pre-treatment of 5 min affected a maximum power density 2.5 times higher than the untreated sludge. Moreover, in our previous study, using batches, we examined the effect of ultrasonication on eliminating methanogenesis and therefore enhancing the biohydrogen production [31]. The optimized sonication energy for hydrogen production using anaerobically digested sludge was 79 kJ/g TS and the hydrogen yield increased by 45% compared with the untreated sludge.

It is indeed intriguing that despite the well established enhancement of biohydrogen production by degassing alluded to above, and the positive influence of ultrasonication on mass transfer, no single study attempted to explore the use of ultrasonication inside continuous biohydrogen systems. Thus, the primary objective of this study was to explore the impact of ultrasonication on biohydrogen production in a new sonicated biological hydrogen reactor (SBHR) and compare it with the most common bioreactor, the continuous stirred tank reactor (CSTR).

Table 1 – Different gas sparging in CSTR, adapted from Kraemer and Bagley [12].

Sparge gas	H_2 yield mol H_2/mol hexose		Yield increase (%)	Ref.
	No sparging	With sparging		
N_2	0.85	1.43	68	[11]
N_2	1.26	1.87	48	[13]
N_2	0.9	1.5	66	[14]
N_2	1.23	1.65	34	[15]
N_2	0.77	0.95	23	[16]
N_2	1.3	1.8	38	[17]
CO_2	0.77	1.68	118	[16]
CH_4	Not reported	Not reported	88	[18]
Biogas	0.77	0.86	12	[16]

2. Material and methods

2.1. Systems set up and operation

Two continuous-flow completely mixed reactors (10 cm diameter, 30 cm height) with a working volume of 2 L each were used in this study (Fig. 1). One is a conventional continuous stirred tank reactor and the other one is the sonicated biological hydrogen reactor (SBHR) which comprised a conventional continuous stirred tank reactor connected with a lab scale 2.5-inch diameter ultrasonic probe at the bottom of the reactor (1 cm above the bottom of the reactor). The sonication pulses (inside the reactor) were set to 1 s on and 59 s off. The ultrasonic probe was supplied by Sonic and Materials (model VC-500, 500 W, and 20 kHz). These two systems (CSTR and SBHR) were operated on synthetic glucose-based feed for 90 days. The two reactors were seeded with 2 L of anaerobically digested sludge and maintained at a constant temperature of 37 °C. After seeding, the two reactors were first operated in a batch mode for 24 h, after which the reactor was shifted to the continuous-flow mode with a hydraulic retention time (HRT) of 12 h. A summary of the operational conditions is shown in Table 3. The two systems were operated at two organic loading rates (OLRs): OLR-1 of 21.4 g COD/L.d with an influent glucose concentration of 10 g/L and OLR-2 of 32.1 g COD/L.d with an influent glucose concentration of 15 g/L.

2.2. Inocula and media compositions

Anaerobic sludge was collected from the primary anaerobic digester at St Mary's wastewater treatment plant (St Mary's, Ontario) and used as seed sludge after sonication. The total suspended solids (TSS) and volatile suspended solids (VSS) concentrations of the sludge were 11 and 9 g/L, respectively. In order to enrich hydrogen-producing bacteria, the sludges were sonicated using a lab scale sonication device at specific energy of 20 kJ/g TS with temperature control as described in Elbeshbishy et al. [31]. The feed containing glucose at two different concentrations of 10 g/L (Phase 1) and 15 g/L (Phase 2), was supplied by 5 mL/L of a nutrient stock solution with the following composition per liter of stock: 1000 g $NaHCO_3$, 280 g NH_4Cl, 250 g of K_2HPO_4, 100 g of $MgSO_4 \cdot 7H_2O$, 10 g of $CaCl_2 \cdot 2H_2O$, 2 g of $FeCl_2 \cdot 4H_2O$, 0.05 g of H_3BO_3, 0.05 g of $ZnCl_2$, 0.03 g of $CuCl_2$, 0.5 g of $MnCl_2 \cdot 4H_2O$, 0.05 g of $(NH_4)_6Mo_7O_{24}$, 0.05 g of $AlCl_3$, 0.05 g of $CoCl_2 \cdot 6H_2O$, and 0.05 g of $NiCl_2$.