Biohydrogen Production from Organic Solid Waste in a Discontinuous Process

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ABSTRACT

The organic solid waste (OSW) represents more than 60% of total urban waste and include 75% of easy-to-degrade matter. Using a fermentative process, the organic matter is transformed into H_2, CO_2 and organic acids and alcohols, this make feasible the biological production of H_2. There exist several parameters that affect the H_2 production as the hydraulic residence time (HRT). In order to optimize the process is necessary to determine the HRT where the H_2 production is maximized. The objective of this study was to evaluate the effect of HRT on H_2 production form OSW in a Sequencing Batch Reactor (SBR). Different HRT (72, 24, 12 and 6 h) were evaluated in an SBR of 1.25L (with a head space of 250 mL and an exchange volume of 50%). Each HRT was maintained in the reactor at least 10 degradation cycles. OSW at 5gVS/L was filled as substrate at each degradation cycle. The reactor was inoculated with fermentative H_2 producers selected by a thermal shock pre-treatment (103-105 °C during 1 h). H_2, CO_2, methane and Volatile Fatty acids (VFA) were determined by gas chromatography. Kinetics of H_2 production was adjusted to the Gompertz model. The results showed that the values for H_2 in biogas varied from 22 to 48% depending the HRT. The highest H_2 production was obtained applying an HRT of 24 followed by the HRT of 12 h. The maximum H_2 percentage in gas (48 ± 6 %), maximum volumetric H_2 production (757 ± 391 mL H_2) and the maximum H_2 production rate (328 ±144 mL H_2/h) were obtained at HRT of 24 h. Acetic acid was the main VFA obtained. Higher propionic acid production was observed at HRT of 6h, reducing the maximal H_2 generation to 282 ± 24.

Keywords: Bio-hydrogen; HRT;organic solid waste.

1. Introduction

Hydrogen (H_2) is considered an energy vector that has a high heat capacity (33.3 - 39.4 kWh / kg) compared to other fuels [1]. It is possible to produce H_2 from organic waste, biomass and/or waste water through a dark fermentation using microorganisms, which has proven to be a relatively simple and inexpensive process [2]. One kind of waste that can be used in the hydrogen production is the organic solid waste (OSW). The OSW represents an environmental problem, particularly in large cities where the typical methods of disposal are landfills or open dumps. The OSW is mainly composed of carbohydrates (rich components cellulose and starch), lipids and proteins, all of these complex polymers are useful for fermentation. Therefore, it is possible to degrade the OSW and obtain H_2 as a value-added product [3].

The application of the hydrolytic-acidogenic stage of the anaerobic digestion process is an appropriate alternative to produce hydrogen and to obtain an effluent rich in dissolved organic matter, composed by volatile fatty acids, (VFA), mainly acetic, propionic and butyric acid, lactate and solvents (acetone and ethanol). The H_2 production yields are closely related to the fermentation pathway and end-products [1,4].

One of the main factors affecting the production of H_2 is the hydraulic residence time (HRT). Different HRT has been reported depending the OSW origin and reactor operation mode for H_2 producing reactors, these time ranging from 5 to 144 h [2,5]. This parameter affects the fermentation metabolism, microbial composition and activity. It has been reported that short HRT promoted the H_2 production, and can be used for washing of methanogenic microorganisms in the fermentative reactor. Because of this, it is necessary to determine the optimal HRT for the highest production of H_2. For this reason, the aim of this study focuses on evaluating different HRT in a sequencing batch reactor (SBR) to produce H_2 using OSW as substrate.

2. Experimental

The OSW was obtained from the main cafeteria at the UNAM campus Juriquilla, in Queretaro, Mexico. The collected residues was characterized by NMX-AA-015-1985 standard [6]. Some non-fermentative residues were discarded including inert material (paper and plastic) and bones, with this only the fermentable material was preserved. Sampling was performed during three weeks and the OSW were refrigerated at 4 °C for preservation. In each collection, bones and inert material (paper and plastic) were discarded; only the fermentable matter was preserved. The collected residue was triturated with the help of a blender to homogenize the particle size (<0.5 mm), then frozen at -20 °C until use.

An SBR reactor constructed of acrylic material with a working volume of 1L and an exchange volume of 50% was used. The biogas collection and measurement was performed by the brine displacement method, with an inverted cylinder and characterization of biogas by gas chromatography (Varian 8610 SRI C). The reactor remained constant agitation and constant temperature (35-37 °C).

Anaerobic granular sludge from a UASB reactor of a brewery industry was used as inoculum. The reactor was inoculated with 16 g/L of thermally pretreated sludge (103 - 105 °C for 24 h) equivalent to 26.7 gTS/L. The reactor was operated under four different HRT: 72, 24, 12 and 6 h. Due to the low alkalinity of the OSW a mineral solution and citrate buffer (1M) was added to avoid acidification of the medium due to the presence of VFA according to [3]. The initial pH was adjusted at the beginning of each feeding cycle to a value of 7. The COD_{total}, Total and volatile solids (TS and VS) and NH_3 were determined according to the Standard methods [7].

The calculations for the kinetic analysis was performed based on the cumulative hydrogen production production obtained. The modified Gompertz equation (Eq. 1) was used for data analysis [3].

$$H(t) = H_{max} * \exp\left[-\exp\left(\frac{2.71828 * R_{max}(\lambda - t)}{H_{max}} + 1\right)\right] \quad (1)$$

Where, H(t) ($mL/L_{reactor}$) is the total amount of hydrogen produced at culture time t (h); H_{max} ($mL/L_{reactor}$) is the maximal amount of hydrogen produced. Rmax ($mL/L_{reactor}/h$) is the maximum hydrogen production rate; λ (h) is the lag time before the exponential hydrogen production.

Microbial characterization of the reactor at HRT of 24 and 12 h was obtained by a pyrosequencing analysis was performed using a Roche Genome Sequencer FLX Titanium system. The 16S rRNA genes were amplified with primer set 515 forward and 806 reverse Sequences were analyzed using the Quantitative Insights into Microbial Ecology (QIIME) software [8]. OTUs were defined using the UClust algorithm on the basis of 97% sequence identity. Reads were classified using the Classifier tool from the Ribosomal Database Project, setting the bootstrap cutoff at 50%.

3. Results and discussion

The characterization of the OSW of the university cafeteria showed that there is great variation in the fractions depending the menu, in this sense, the values of different fractions is presented: Fruits and Vegetables 62.7±16.1 %, Meat 8.2±7.2 %, flour (including pasta, tortillas and bread) 13.9 ± 8.0%, and others (mixed residues difficult to separate in the other groups e.g. eggshell, etc.) 15.17±16.0%. After performing grinding and homogenization of the various samples days, a homogenous mash was used as reactor feed. The feed for the SBR showed the following values: moisture 82%, TS 203 g/L, Fixed solids 48 g/L, VS 155 g/L, density 1115 kg/m^3, COD_{total} 336 g/L, 400 mg NH_3/L and alkalinity 8 g/L of $CaCO_3$. Due to the low alkalinity, it was necessary to add a buffer solution to prevent and mineral acidification reactor.

The reactor was operated for 60 cycles. The initial HRT was 72 h (cycles 1 through 9) and was subsequently decreased to 24h (cycles 10 to 20), 12 h (cycles 21-43) and 6h (cycles 44-59). Figure 1 shows the percentages of H_2, CO_2 and methane in the biogas during operation of the bioreactor. It is observed that after 72 h the highest percentage of H_2 was 44.1±12.0% at 24, 12 and 6 h the percentage reported is 52.6 ±6.0, 44.2±13.03 and 42.1±14.1%, respectively.

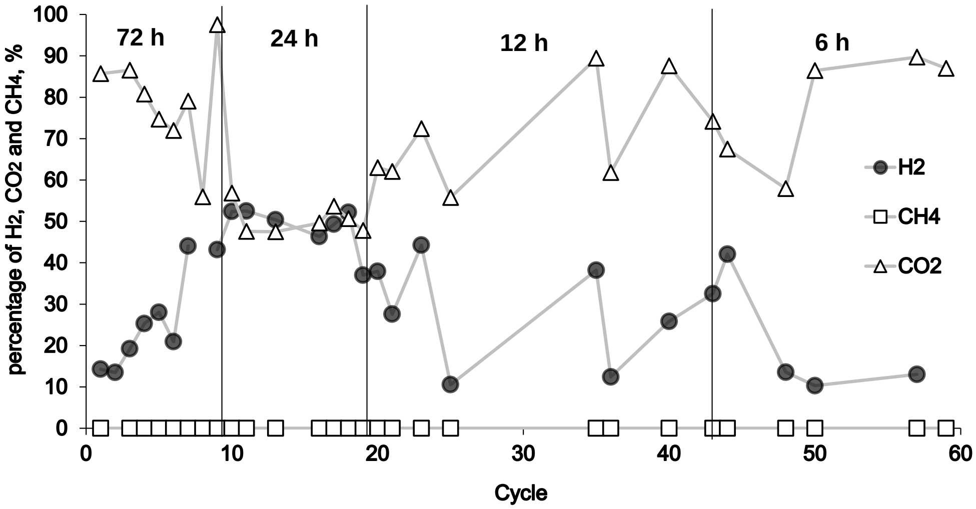

Fig 1. Percentage of hydrogen, CO_2 and methane in biogas at different HRT.

The general behavior observed in the hydrogen production kinetics at different HRT evaluated is shown in Figure 2. It is possible to observe that there higher H_2 production was produced during HRT of 24 h and 12 h (24.6 and 22.3mmolH_2/ h), while than for cycles 72 and 6 h the maximum production was 8.5 and 7.6 mmolH_2/h, respectively.

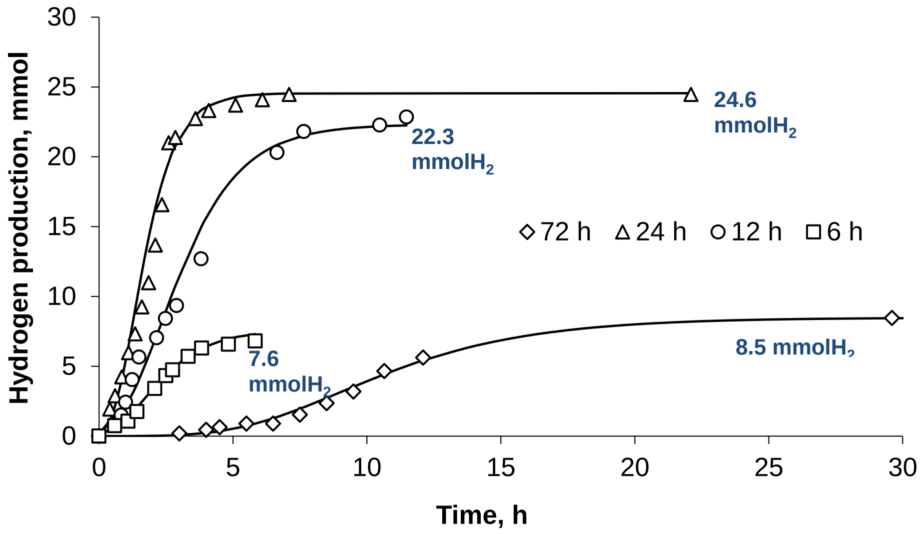

Fig 2. Hydrogen production kinetics at different HRT

The higher hydrogen production per gram of VS was obtained applying an HRT of 24 h (15.2 mmolH_2/g$VS_{removed}$). The maximum production in the case of HRT of 72, 12 and 6 h was 2.5, 4.4 and 1.6 mmolH_2/g$VS_{removed}$, respectively. The specific hydrogen production rate of (SHPR) for different HRT in this study is shown in Figure 3. I was observed that higher SHPR was obtained at 24 h. The average values for SHPR were 0.53±0.19, 8.5±4.1, 5.6±4.0, 5.1±1.4 mmolH_2/gVS/d for HRT of 72, 24, 12 and 6 h, respectively.

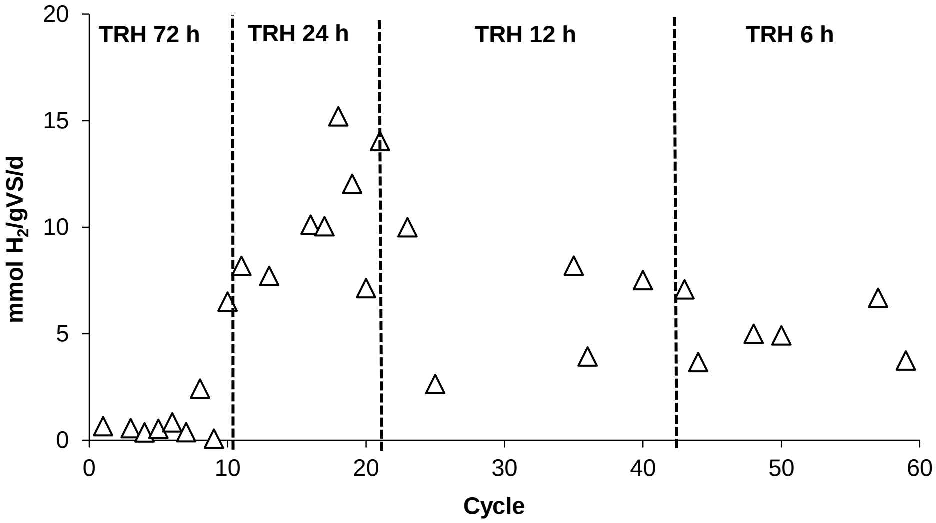

Fig 3. The specific hydrogen production rate for different HRT.

The principal VFA produced was the acetic acid. The higher acetic, butyric, isovaleric, acetone and ethanol production was obtained at 24 h and is related with the high hydrogen production. For the case of the propionic acid, the higher production was obtained in a HRT of 6h. This increase in the propionic acid is correlated with the decrease in the hydrogen production since this VFA consume H_2 to be produced. It has been reported that if the process is mainly oriented to acetic and butyric acid production pathway, the H_2 production can be maximized [4].

Table 1. Volatile fatty acids, acetone and ethanol production for the different HRT evaluated.

HRT	Concentration (*g/L*)						
(*h*)	Acetic	Propionic	Butyric	Isobutyric	Isovaleric	Acetone	Ethanol
72	4.30 ± 1.70	0.72 ± 0.37	2.46 ± 1.89	0.45 ± 0.26	0.34 ± 0.08	0.27 ± 0.13	0.85 ± 0.45
24	5.77 ± 4.06	0.46 ± 0.16	4.13 ± 3.86	0.82 ± 0.35	0.46 ± 0.07	0.80 ± 0.41	1.51 ± 1.17
12	2.37 ± 2.80	0.90 ± 0.18	0.90 ± 0.13	0.015 ± 0.0	0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.01
6	2.97 ± 0.17	1.29 ± 0.14	1.05 ± 0.01	0.07 ± 0.05	0.07 ± 0.01	0.02 ± 0.01	0.02 ± 0.02

The microbial characterization demonstrate the phylum Firmicutes represent more than the 99% of the OTUs found in the sample of the reactor. The family Veillonellaceae represent 99% of the OTUs of the Firmicutes. The Veillonellaceae are a family of the Fimicutes and Clostridia class. Members of this family are all obligate anaerobes and occur in habitats such as rivers, lakes, and the intestines of vertebrates. it has been reported that this family could contribute to greater hydrogen production at low OLRs using easy-to-degrade substrate (as glucose) and lactate [9]. The genus Megasphaera represent 88% of all the OTUs obtained in the analysis, i.e., the dominant genus in the microbial community. Megasphaera sp. was reported to be present in hydrogen production in reactors and also reported in fermentation including Ethanol + butyrate and ethanol type fermentation [10,11].

4. Summary and perspectives

The results showed that the values for H_2 in biogas varied from 22 to 48% depending the HRT. The highest H_2 production was obtained applying an HRT of 24 followed by the HRT of 12 h. The maximum H_2 percentage in gas (48 ± 6 %), maximum volumetric H_2 production (757 ± 391 mL H_2) and the maximum H_2 production rate (328 ±144 mL H_2/h) were obtained at HRT of 24 h. Acetic acid was the main VFA obtained. Higher propionic acid production was observed at HRT of 6h, reducing the maximal H_2 generation to 282 ± 24 mL. The genus Megasphaera showed to be the dominant genus in the microbial community.

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