Start-up of Continuous Stirred-Tank Reactor for Biohydrogen Production from Restaurant Organic Waste

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ABSTRACT

Recently, continuous stirred-tank reactor (CSTR) has been applied to degrade organic solid waste (OSW) in anaerobic digestion. If the anaerobic process is separated in two phases (hydrolytic-acidogenic and methane production steps), it is possible to increase the energy production due to the hydrogen (H_2) generation in the first step. The objective of this study was to star up and operation of a CSTR to generate H_2 from food waste of a restaurant in order to determine the operational conditions for increase the H_2 production. The start-up was obtained in three phases: 1) Inoculum activation with glucose, 2) Acclimation of inoculum to H_2 production in a discontinuous process and 3) CSTR operation. The reactor was constructed by acrylic with a total useful volume of 2 L with a headspace of 0.3 L. The hydraulic residence time (HRT) was fixed in 24 h and the organic loading rate (OLR) was of 22 g TS/$L_{reactor}$/d. The reactor was inoculated with anaerobic sludge from a brewery. Fermentative H_2 producers selected by a thermal shock pre-treatment (103-105 °C during 24 h). H_2, carbon dioxide (CO_2), methane (CH_4) and Volatile Fatty acids (VFA) were determined by gas chromatography (GC). H_2 production was 365mL H_2/$L_{reactor}$/d and H_2 yield was 19 ml H_2/g SV. CH_4 was not detected. The total solid (TS), volatile solid (VS), and chemical oxygen demand (COD) removal was 42.8±6.3 and 50.9±6.4 and 24.1±10.7 respectively. The removal carbohydrate (80%) was bigger than proteins (24%).

Keywords: CSTR; bio-hydrogen; organic solid waste, organic loading rate, hydraulic residence time

1. Introduction

The H_2 has been widely recognized as an alternative energy source to substitute fossils fuels. This is a clean fuel, it can be used in fuel cells to produce electrical energy where only water is produced as a byproduct, and because H_2 has high specific energy content (33- 39.4 kWh/kg) compared and other fuels [1-4]. Among the H_2 production methods, the most promoting and friendly method is dark fermentation from organic solid waste, especially food waste [2].

Dark fermentation is a biological process where a microbial consortium degrades the organic matter at anaerobic condition to produce biogas composed with the H_2 and CO_2 and a digestate rich in volatile fatty acids that can be used in other biological processes as photofermentation. However, dark fermentation is a step intermediate in anaerobic digestion. Anaerobic digestion is performed in four stages; hydrolysis, fermentation, acetogenesis and methanogenesis [1]. Thus, H_2 is a key intermediate consumed mainly in methanogenesis by archeas methanogenic. Therefore, for producing H_2 would inhibit methanogens. Methanogen inhibition is possible by means of a biokinetic control and heat-shock treatment. Biokinetic controls refers to the control of pH during operation, usual used pH between 5-6, the use of low HRT in continuous reactor to eliminate microorganism growth rates below the rate of dilution as the archeas methanogenic [8]. The theory of the method of treatment by thermal shock is based on the thermal shock that can inactivate methanogenic archaea and cultivate fermentative spore-forming bacteria such as *Clostridium* sp. [7].

It has been reported the H_2 production from biological fermentation of organic fraction of solid waste especially food waste. Food waste is a carbohydrates rich waste; this can be used in the dark fermentation to produce H_2. This available waste has high organic matter content and they are low cost [4,7-9].

In 2006 was reported the study of H_2 production in continuous stirred-tank reactor (CSTR) from food waste the production of H_2 from organic solid wastes from home in a CSTR. The operating conditions were organic loading rate of 37.5 g VS / $L_{reactor}$ / d, HRT 2 d, pH 5.2 and mesophilic conditions at 35 ° C. The H_2 production rate was 1.6 L $H_2/L_{reactor}$/d and H_2 yield 43 ml H_2/g SV [4].On other hand, in 2009 was reported the study of H_2 production in a semi-CSTR. The operating conditions were organic loading rate of 22.5 g VS / $L_{reactor}$ / d, HRT 6.7 d, pH 5.5 and mesophilic conditions at 40 ° C. The H_2 production rate was 1.4 L $H_2/L_{reactor}$/d and H_2 yield 65 ml H_2/g SV [9].

The objective of this study was to evaluate the start-up and operation of a CSTR for bio H_2 production from the organic fraction of restaurant food waste at mesophilic conditions and at low concentration of initial total solids in order to determine the operational conditions for increase the H_2 production.

2. Experimental

2.1. Inoculum

Anaerobic granular sludge from an anaerobic sludge blanket reactor treating brewery wastewater was used as inoculum. The sludge was pretreatment whit thermal shock at 105°C during 24 h in order to inhibit the activity of methanogen archeas and to select hydrolytic and fermentative bacteria (mainly related to microorganisms of genus *Clostridium*) [7].

2.2. Food waste

Food waste was obtained from a restaurant in the city of Querétaro, Mexico. Waste was collected during 7 days, physically characterized and store a 4°C. In each collection, the citrus waste, bones and inert material (paper and plastic) were discarded; only the fermentable matter was preserved. The physics compositions of the food waste was fluor waste 30±8%, citrus waste 22±4%,fruits and vegetable waste17±4% and meat waste 10±3.

After selecting the food waste, it was crushed and homogenized in a grinder JR MJ22 ® of 1HP. After, the particle size less than 5mm was obtained in a sieve. Finally food waste was frozen at -20°C until it was used. The physics and chemical characteristic of the food waste used in this study are showed in table 1.

Table 1. Characteristic of raw food waste

Parameters	Food Waste
Moisture (%)	75.7±4.6
TS (%)	24.3±4.6
VS (%)	20.8±2.3
COD (g/kg)	344.7±35.3
Carbohydrates (g/kg)	59.6±2.7
Proteins (g/kg)	108.1±8.3
Density (kg/m^3)	1097.6±29.7
pH	4.4±0.01

2.3. Set-up and operation

The start-up of CSTR for H_2 production was obtained in three phases: 1) Inoculum activation with glucose, 2) Acclimation of inoculum to H_2 production in a discontinuous process and 3) continuous operation. The inoculum was activated for 48 h whit glucose in aqueous prepared with 10 g/l of inoculum, 5 g/L of glucose, 0.3 g/L of K_2HPO_3, 0.4 g /L of NH_4Cl, 20 ml/L of solution mineral A and B prepared as show in [7], in a sequential batch reactor (SBR) at mesophilic conditions 37°C and agitation of 70 rpm.

The inoculum activated was acclimatized to the food waste in discontinuous mode for two cycles of 24 h. The reactor was operated with the following operating conditions temperature 35°C, pH 5.5, ST 22 g/L and agitation of 70 rpm. After the end of the second cycle of the SBR operation, the operation mode was switched to continuous operation until steady state was reached. The operating conditions were the following: hydraulic residence time (HRT) 24 h, organic loading rate (OLR) 22 g of TS/$L_{reactor}$/d, at 35 °C, pH of 5.5, reaction volume of 1.7 L and feed and discharge flow of 1.7 L / d.

The experimental set-up is show in figure 1. It consisted of one 2L reactor whit 1.7 L working volume. Food waste whit a concentration of 2.2 % of TS was added at CSTR with a peristaltic pump Cole Parmer System 7553-12 ®. The substrate was added from a storage tank at 4°C with a peristaltic pump Cole Parmer System NO-7553-12 ®.

The pH in the reactor was maintained at 5.5 ±3 by a controller pH Black Stone BL931700®. It was coupled to a peristaltic pump Marlow Watson 120U®. Peristaltic pump added Sodium hydroxide (NaOH)

2 N when the pH dropped until 5.4 and stopped when the pH achieved 5.5.The temperature in the reactor was maintained at 37°C via water bath through water jacket surrounding the reactor.

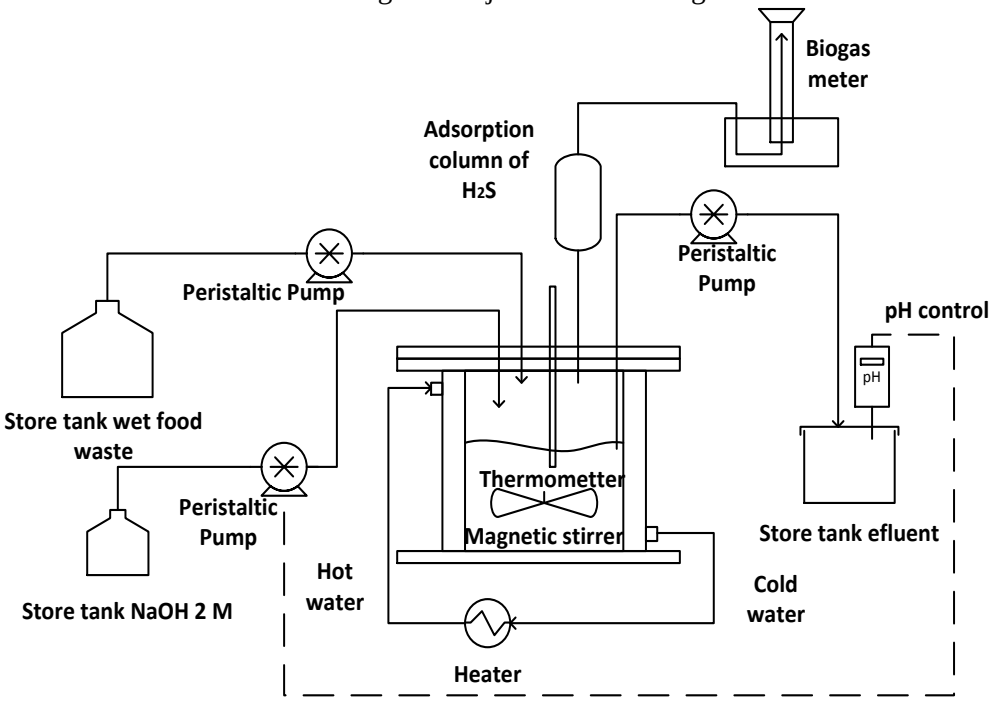

Fig 1. Schematic diagram of H_2 production process

H_2S was removed from biogas with an adsorption column. The adsorption column packed with ferric oxide (Fe_2O_3). The measurement of biogas production was done by liquid displacement method. This method consisted of measure fluid volume displace in an interval time.

2.4. Analytical techniques

TS, VS, COD, protein and carbohydrates were determined according to the procedures described in Standard Methods [11]. The percentages of H_2 and CO_2 in the gas phase were determined using a gas chromatograph (GC) SRI8610C® equipped whit a thermal conductivity and column packet. The operation temperatures of the injector port, the column and detector were 156, 41, and 156°C, respectively. Nitrogen was used the carrier gas at the flow rate of 30ml/min. VFAs (acetic, propionic, isobutyric, butyric and isovaleric), solvents (ethanol and acetone) were determined by GG with flame ionization detectors (FID) and column packet. The operation for the injection port, the oven, and the FID were 190, 70, 210 respectively. Nitrogen flow rate was 2.5 ml/min

3. Results and discussion

The activation with glucose was obtained in 3 d, H_2 accumulative production was 858 ml. In this phase only fermentative bacteria which use glucose as substrate were selected and hydrolytic bacteria were not

activated. The reactor was operated in mode SBR during two cycles of 24h. In the first cycle was produced 157 ml $H_2/L_{reactor}/d$ and the second cycle was produced 137 ml $H_2/L_{reactor}/d$.

The CSTR of H_2 production was operated in the laboratory forty days. The profile of H_2 production rate and volatile fats acids production shown in the figure 2. H_2 was produced immediately from the first day; however, H_2 production rate declined drastically from day 1 to 3 of 530 to 4 $ml/L_{reactor}/d$. This drop is due to the change of substrate and type of operation.

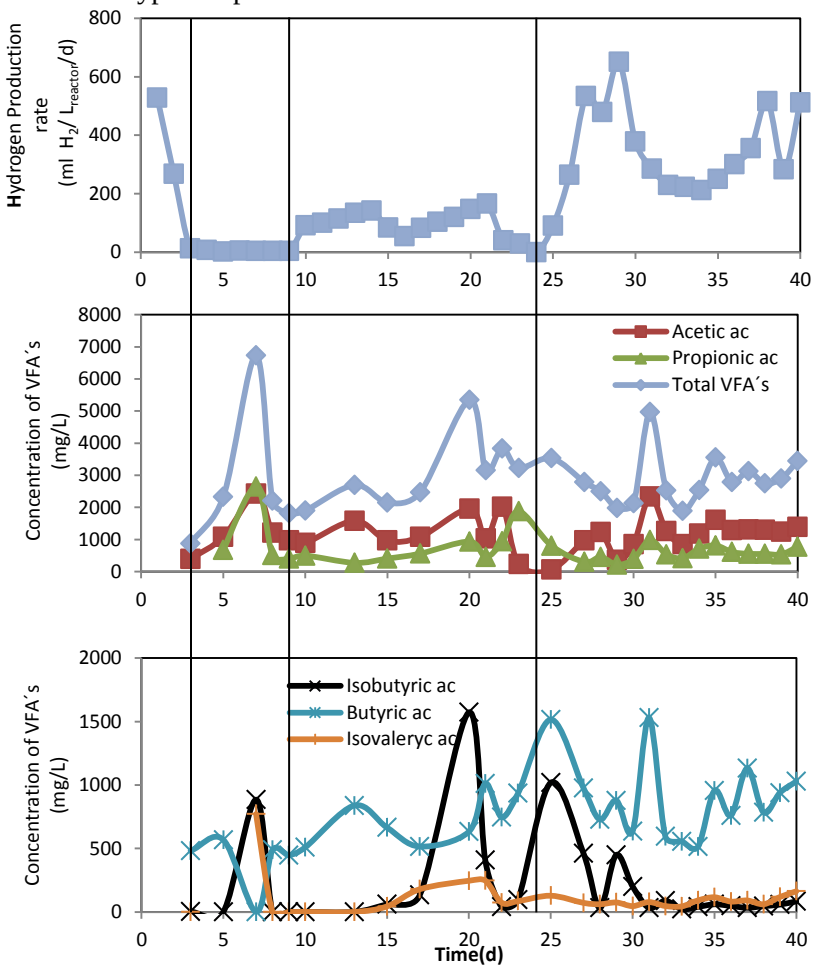

Fig 2. Profile of H_2 production rate and volatile fats acids concentration(ac: acids)

Between the day 3 and 9 the H_2 production was very low and fluctuated between 4-12 $ml/L_{reactor}/d$. This time was an adaptation phase hydrolytic and fermentative bacteria. In this phase the VFA´s concentration was 2794±144 mg/L. The acetic and propionic acids concentration were the highest concentration presented 1217±1062 and 1060±395 respectively. Isobutyric, butyric and isovaleric acids showed a lower concentration 178±395, 397±226 and 193±386 mg/L respectively.

For the 10 day and 21, H_2 production rate increase to 100±40 $ml/L_{reactor}/d$. In this period of time, a large amount of lipids was accumulated inside the CSTR (in the top part of the surface, between the

fermentation phase and the headspace). This caused a decrease in the mass transferer between the reaction and the headspace producing a decrease in H_2 production between days 21 to 24. During this period the concentration the total VFA´s was 3267±2274 mg/L. In this period of time, acetic, propionic and butyric acids concentration were the highest concentration presented 1269±632, 780±547 and 763±17 mg/L respectively. Isobutyric and isovaleric acids showed a lower concentration 330±564 125±99 mg/L respectively.

In the day 24, the lipids were removed inside CSTR, and then H_2 production rate increase between days 25 to 40. During this period, the H_2 production rate was approximately 338±151 ml/$L_{reactor}$/d. In this time acetic and propionic acids was produced in higher concentration (1230±441 and 858±270 ml/$L_{reactor}$/d respectively) than propionic, isobutyric and isovaleric. The concentration the total VFA´s was 2850±780 mg/L.

The profiles of H_2 yield and organic load removal are shown in the figure 3. The profile of H_2 yield presented a similar behavior compared with the profile of H_2 production rate. H_2 yield dropped between days 1 and 3, during the day 3 to 9 the average H_2 yield was 0.2±0.19ml H2/g SVadd. Between days 10 and 23 H_2 yield was 4.8±2.6 ml H_2/gVS_{added}. The maximum H_2 yield 19.2±16 ml H_2/g SV_{add} was presented between days 25 and 40.

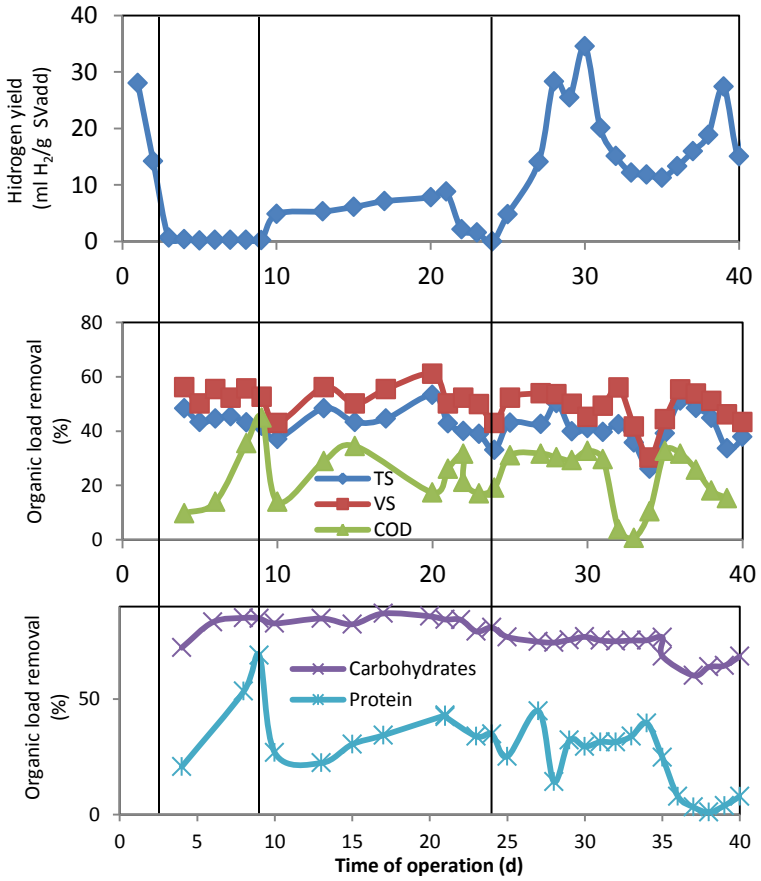

Fig 3. Profile of H_2 yield and organic load removal

However, removal of TS and VS varied in a range of 26% to 54% and 40% to 60 %, respectively. Average removal of ST and VS was 42.8±6.3 and 50.9±6.4 percent respectively. Removal carbohydrates 77.1±7% were bigger than removal proteins 26.7±17. Removal carbohydrates varied in a range slightly constant 60 to 84% compared whit protein.

In this present study, maximum H_2 yield and production was less than similar study with food waste (table 2). This difference can be related to the differences on operation condition. The H_2 production rate was 36% that is similar to other reports [4,9]. It is important to note that the inoculum, OLR and HRT applied are different in each study.

Table 2. Examples of maximum H_2 yield and production from food waste in CSTR

Source	[4]	[9]	This study
Type reactor	CSTR	Semi-CSTR	CSTR
Substrate	Food waste	Food waste	Food waste
Inoculum	Anaerobic sludge	Microbial cultures contained in food waste	Anaerobic granular sludge
T (°C)	37	40	35
pH	5.2	5.5	5.5
HRT (d)	2	6.7	1
OLR (g VS/L/d)	37.5	22.5	18.7
H_2 (ml $H_2/L_{reactor}/d$)	1600	1462	533
Yield (ml $H_2/g\ VS_{added}$)	43	65	28

4. Conclusions

The start-up of the reactor for H_2 production from food waste demonstrated working successfully reaching a H2 production of 365mL $H_2/L_{reactor}/d$ and H_2 yield was 19 ml H_2/g SV. Stoichiometric relationships between H_2, acetate and butyrate in the really dynamic fermentation are observed in this study. The accumulation of lipids inside CSTR produced a negative effect on the production of H_2. The total solid (TS), volatile solid (VS), and chemical oxygen demand (COD) removal was 42.8±6.3 and 50.9±6.4 and 24.1±10.7 respectively. The removal carbohydrate (80%) was bigger than proteins (24%)

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