CHEMICAL ENGINEERING TRANSACTIONS

VOL. 74, 2019

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza

ISBN 978-88-95608-71-6; **ISSN** 2283-9216

DOI: 10.3303/CET1974031

Continuous Multiple Tube Reactor in the Hydrogen Production Using Sucrose

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Biohydrogen ($BioH_2$) is considered a promising fuel characterized by the high energetic content per unit of mass, easy electricity production by fuel cells (FCs), which generate water as the only by-product. The objective of this study was to evaluate the performance of a continuous multiple tube reactor (CMTR) with the inner surface of the tubes as worm thread in the continuous production of hydrogen. The useful volume of the reactor was 1065.5 mL. The reactor was operated under anaerobic conditions, continuous upflow and kept in an air-conditioned chamber at 25 ºC. Two assays were conducted: E1: COD of 2 g L^{-1}, hydraulic retention time (HRT) of 2 h and organic loading rate (OLR) of 24 g $L^{-1}d^{-1}$; E2: COD - 4 g L^{-1}, HRT – 2h, OLR - 48 g COD $L^{-1}d^{-1}$. The monitoring to evaluate the reactor performance included chemical oxygen demand (COD) removal efficiency (ER_{COD}, %); sucrose conversion efficiency (EC_{suc}, %); biogas flow rate (Q_{biogas}, in mL h^{-1}); hydrogen molar flow (MHFR, in mmol H_2 h^{-1}), hydrogen yield (HY, in mol H_2 mol^{-1} sucrose) and volumetric hydrogen production rate (VHPR, in mL H_2 L^{-1} d^{-1}). The CMTR presented stability in H_2 production, which allowed the production for long operation periods. The adaptation of the inner surface of the tubes as worm thread improved the performance of the system, which indicates that the biomass retention was sufficient to attend the conditions of the system.

1. Introduction

It is possible to affirm that there is a strong global tendency to prioritize researches and to development technologies that use renewable sources to contribute with the environmental sustainability. Among the alternatives, hydrogen technologies are considered the successors of fossil fuels, since it presents significant energetic value. Compared with conventional fuels, $BioH_2$ produces water as the only by-product, which means lower productions of pollutants. The hydrogen (H_2) production presents four basic processes of non-fossils energy primary sources: (i) water electrolysis; (ii) thermochemical, (iii) radiolytic and (iv) biological processes (SHAHLAN et al., 2018). The anaerobic fermentation has been highlighted among the biological processes for H_2 obtainment, especially for the higher production of this gas when compared to other biological processes; besides, there is the possibility of using and treating different residual materials as substrate (HAFEZ et al., 2010; HASYIM et al., 2011; LEE et al. 2008; WEI et al., 2010; DE SÁ et al., 2014). Hydrogen production by fermentative processes is largely approached in the literature on different reactors, especially in continuous process and batch operation. However, many researches has reported the maintenance difficulties on the continuous production and high hydrogen rates for long operational periods. It should be noted that there are many factors that could affect the continuous hydrogen production, such as pH, hydraulic retention time, temperature, carbon source, organic loading rate (OLR), metabolic paths and microbial diversity. Some studies have indicated that the instability on hydrogen production could be related with the OLR of food-to-microorganism ratio (F/M), which could reach values that impair hydrogen production with the increase of biomass in the reactor (ANZOLA-ROJAS et al., 2013; HAFEZ et al., 2010).

Paper Received: 28 April 2018; Revised: 22 September 2018; Accepted: 8 December 2018

Please cite this article as: Trevisan A.P., Lied E., Devens K., Tonello T., Biasotto G., Rossi L., Fernandes J., Gomes S., 2019, Continuous Multiple Tube Reactor in the Biohydrogen Production Using Sucrose, Chemical Engineering Transactions, 74, 181-186 DOI:10.3303/CET1974031

In this regard, Gomes et al. (2015) proposed the continuous multiple tube reactor (CMTR) as alternative to overcome the limitations related to the specific organic loading rate (SOLR) aiming the continuous biomass discharge through the implementation of elevated superficial velocities in the tubes. However, the biomass retention in the system was low, which negatively affected hydrogen production. Thus, these authors suggested that the inner surface of the tubes were adapted as worm thread to improve the biomass retention in the reactor. Therefore, in the present study the production of hydrogen in CMT with inner surface of the tubes adapted as worm thread was evaluated using sucrose as carbon source under mesophilic conditions.

2. Material and Methods

2.1 Continuous Multiple Tube Reactor and experimental conditions

The CTMR used in this study was constructed with three compartments, as proposed by Gomes et al. (2015): loading and discharge chambers (manufactured in acrylic) and intermediary region (composed by 12 PVC tubes with external diameter and length of 12 and 680 mm, respectively). The inner surface of the tubes were adapted as worm thread to increase the biomass adhesion to the wall. The reactor useful volume was 1065.5 mL: 80 mL (loading chamber) + 545.5 mL (tubes zone) + 440 mL (discharge chamber). Figure 1 presents the experimental setup and the constructive characteristics of the reactor.

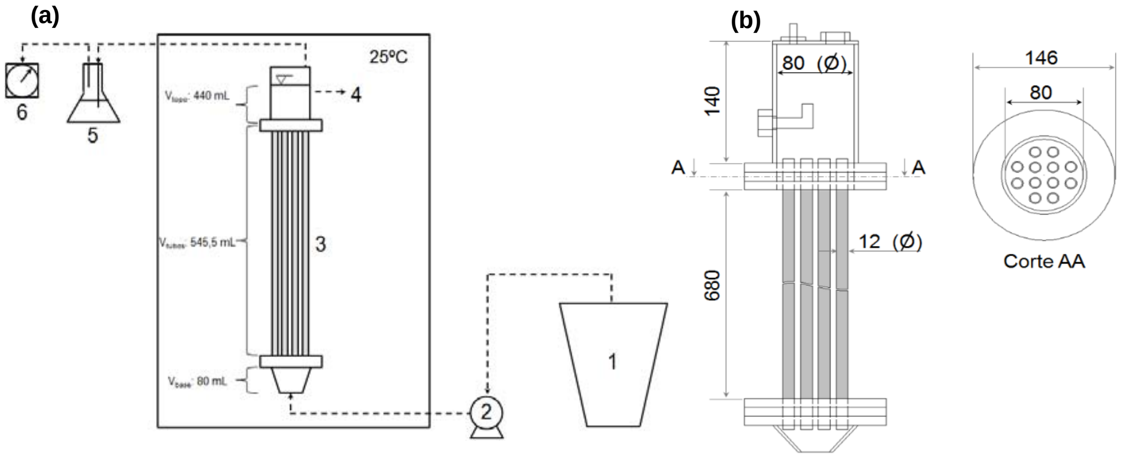

Figure 1 (a) Experimental setup and (b) Reactor constructive characteristics. Notes: 1-Synthetic wastewater reservoir; 2-Peristaltic pump; 3-Multiple tubes reactor; 4-Effluent outlet; 5-water seal; 6 -Gas meter. Source: Gomes et. al (2015)

The reactor was operated with continuous upflow and maintained in an acclimatized chamber at 25° C. The CMTR was fed with synthetic substrate with sucrose as carbon source. Two assays were carried out in the CMTR: assay 1 (E1) – organic loading rate (OLR) of 24 g DQO $L^{-1}d^{-1}$ (DQO affluent of 2000 mg L^{-1}; hydraulic retention time (HRT) of 2 h) and assay 2 (E2) – OLR of 48 g DQO $L^{-1}d^{-1}$ (DQO affluent of 4000 mg DQO L^{-1}; HRT of 2 h). The period of the assays comprehended 96 days.

2.2 Synthetic Wastewater and Inoculum

The synthetic wastewater was based on sucrose (1781.24 mg L^{-1}), urea was used as carbon and nitrogen sources, and nutrients solution (Del Nery, 1987, according to Lima e Zaiat, 2012). The COD of the synthetic wastewater was 2000 mg L^{-1} and the C/N rate was 140 (ANZOLA-ROJAS 2010). The pH was adjusted to 6.5 with the addition of 0.25 mL L^{-1} of hydrochloric acid solution (HCL) 12 M. The inoculum was obtained through natural fermentation in accordance to the method described by Leite et al. (2008). Fifteen liters of synthetic substrate were prepared and maintained in an open vessel to promote the fermentation at room temperature (~25° C). After this period, the substrate was recirculated in the reactor for five days to promote the biomass adhesion to the walls of the tube.

2.3 Analytical methods

The system was monitored with the determination of pH, chemical oxygen demand (COD), total carbohydrates (TC), total suspended solids (TSS), volatile suspended solids (VSS) and volatile fatty acids (VFA) in samples collected four times per week. The pH, COD, TSS and VSS were dermined according to the Standard

Methods for the Examination of Water and Wastewater (APHA, 2012). On the TC determination, the method proposed by Dubois et al. (1956) was used.

The analysis of the acids (acetic, propionic, butyric, formic and lactic) were performed through high performance liquid chromatography (HPLC) in Shimadzu® system equipped with Aminex® column HP-87H (300 mm x 7.8 mm Bio-Rad), CTO-20ª oven at 64° C, CBM-20A controller, UV detector with diodes arrangement SPD-20ª in a 208nm wave length and LC-20AT pump. The mobile phase was composed by ultrapure water Milli-Q (Millipore®) acidified with 0.005 M of H_2SO_4 in a 0.5 $mL.min^{-1}$ flow and injection volume of 20µL (LAZARO et al., 2014; PENTEADO et al., 2013). The samples from the discharge chamber of the reactor were filtered with cellulose acetate membrane with porosity of 0.2 µm and acidified with H_2SO_4 (2 M) solution. The biogas flow was monitored daily with gasometer model MGC-1 V30 (*Ritter*®). For the biogas composition determination, a needle with lock (model Sigma®) to collect 500 µL of gas in the reactor four times a week was used. The biogas constituent parts (hydrogen, carbon dioxide and methane) were determinated through gas chromatography in GC system 2010 (*Shimadzu*®), equipped with thermal conductivity detector (TCD), Supelco Carboxen® column 1010 Plot (30m x 0.53mm extern diameter, 0.30µm of thickness), using argonium as a carrier gas (make-up gas flow of 8 $mL.min^{-1}$). The injector and detector temperature were 220° C and 230° C, respectively. The column-heating ramp was 130° C to 135° C, in a rate of 46°$C.min^{-1}$ during 6 minutes (PENTEADO et al., 2013). The response variables calculated based on the determined parameters were COD removal (ER_{COD}, in %), sucrose conversion (%), biogas flow rate (Q_{biogas}, in $mL.h^{-1}$), volumetric hydrogen production rate (VHPR, in $mLH_2.h^{-1}.d^{-1}$), molar hydrogen flow rate (MHFR, in $mmolH_2.h^{-1}$), hydrogen yields (Y_{H2}, in $molH_2.mol^{-1}$ sucrose) and acids ratio.

3. Results and Discussion

Table 1 shows the mean values of the CMTR performance in E1 and E2 related to the following parameters: sucrose conversion, COD removal, biogas flow and composition (H_2 e CO_2), MHFR, Y_{H2}, and VHPR. Assay 2 (4000mg COD L^{-1}; HRT = 2 h) presented better results for most the parameters. For both assays 1 and 2, the carbohydrates conversion efficiency reached values superior to 65% during all the operating period, which corroborate with the values reported by Fontes Lima e Zaiat (2012) (67.2 to 79.2%).

Comparing the results obtained with the literature, Anzola-Rojas et al. (2013), operating a downflow structured bed reactor fed with synthetic wastewater based on sucrose (OLR of 24 g COD $L^{-1}d^{-1}$) reached the Q_{biogas}, VHPR and Y_{H2} of 131.7 mL h^{-1}, 20.83 $mL.L^{-1}.h^{-1}$ e 0.59 mol H_2 mol^{-1} sucrose, respectively, which could be comparable to E2 (Table 1). The VPHR (48.3 mL H_2 h^{-1} L^{-1}) was similar to Penteado et al. (2013), (47.3 mLH_2 L^{-1} h^{-1}) operating an Anaerobic Packed-Bed Reactor (APBR) in the same conditions of this study. Estevam et al. (2018) reported MHFR of 2.2 mmol H_2 h^{-1} using an anaerobic reactor with mechanical stirring (AnsBBR), fed with brewery wastewater, and obtained results similar to those found in this study.

Pachiega et al. (2018) observed better performance than CMTR operating a batch anaerobic reactor with useful volume of 2L, operated by approximately 169h and fed with 2 g L^{-1} of sucrose. In this case, the Y_{H2} values and carbohydrates consumption were respectively of 0.9 mol H_2 mol^{-1} sucrose and 88.7%.

Table 1: Continuous multiple tube reactor performance in the assays E1 and E2

Assay	ER_{COD} (%)	$EC_{sucrose}$ (%)	$Q_{biogás}$ ($mL.h^{-1}$)	H_2 (%)	CO_2 (%)	MHFR (mmol H_2 h^{-1})	HY (mol H_2 mol^{-1} suc)	VHPR (mL H_2 L^{-1} h^{-1})
E1	19.1	77.7	89.9	61.5	38.5	0.99	0.48	48.3
E2	17.5	65.4	103.7	70.0	30.0	1.84	0.51	67.5

Figure 2 presents the time profiles of the parameters related to hydrogen production during the assays (biogas composition, MHFR, VHPR and HY). In E1, all the parameters presented high instability in the production during the operational period. On the other hand, higher gas production and stability were obtained in E2, compared to the first assay. On both assays, the production was maintained the entire experimental period, which suggests that the H_2 production is possible in this reactor design, especially with the as worm thread in the inner walls of the tubes.The CMTR presented stability on H_2 production, thus allowing the production maintenance for long operational periods. The H_2 production period in the assays was superior to those observed by Anzola-Rojas et al. (2013), Fernandes et al (2013), Lima e Zaiat (2012) and Penteado et al. (2013).

The best CMTR performance in E2 was probably due to biomass retention in the inner walls of the tubes, which was sufficient to supply the biomass requirements in the system. As previously discussed, the biomass concentration in the reactor is a relevant factor for H_2 production, being related in the literature to the Y_{H2} increase with the increase of biomass (HAFEZ et al., 2010). Reactors with no fixed bed or support material could present critical values of biomass retention time in the system, often below the minimum recommended (3h) for H_2 production (HAFEZ et al., 2009). Gomes et al. (2015), operating a CMTR in the same feeding conditions (2 g L^{-1} e HRT 2h), observed that in their assays the hydrogen production decreased gradually in a few days of operation (10 to 24 days), ending by the 30th day. The authors stated that the poor performance could indicate that the inner surface of the PVC tubes probably did not provide adequate conditions for the biomass fixation, as a result, the content of solids was not sufficient to attend the biomass rates in the system.

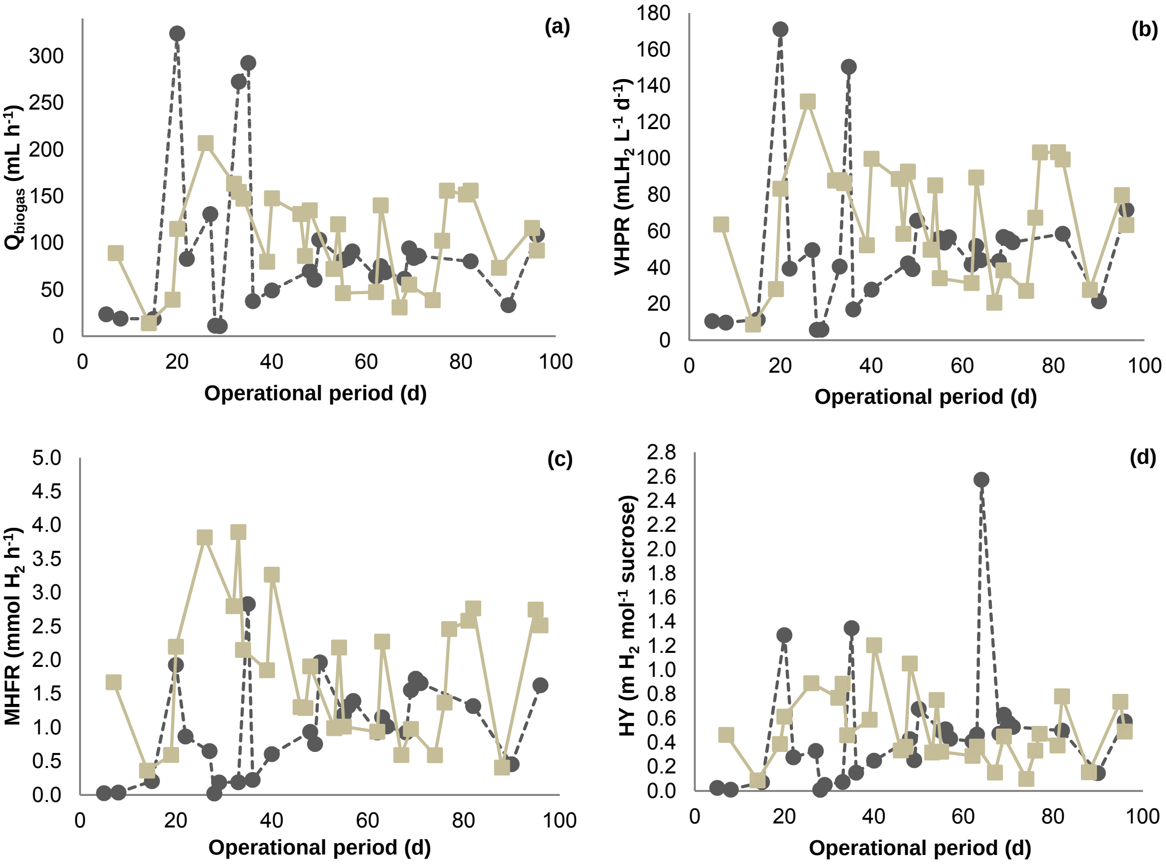

Figure 2 Time profiles regarding biogas and hydrogen production: (a) biogas flow rate, (b) volumetric hydrogen production rate, (c) molar hydrogen flow rate and (d) hydrogen yield. Note: E1 (--●--) and E2 (—■—)

Figure 3 presents the results of the parameters related to sucrose conversion and biomass production in the assays. During operational period, the sucrose conversion was higher in E1 (Figure 3a), with values similar to Anzola-Rojas et al. (2016). The effluent pH was stable, with inferior values on E2 (3.34 - 4.13) (Figure 3b). In the E1, the pH varied from 3.6 to 5.1. The effluent VSS data in the reactor could indicate that the biomass discharge was stable on E2 and relatively unstable in E1 (Figura 3c). These results corroborate those presented in Table 1, which showed the best performance in E2 probably due to high biomass retention in the system. The main metabolites generated on the fermentation in E1 ad E2 were acetic and butyric acid, with low concentrations of formic and propionic acids. The predominance of acid final products during the H_2 production is known to occur in the acidogenic phase, which decreases the pH of the medium.

It is known that low pH values could impair the growth of microorganism. Hence, it has been suggested that the acid absorption (normally followed by the increase of the pH) that occurred during the production phase works as a detoxing process, which initiated in response to the accumulation of acid final products (ZHÃO et al., 2016). Maintinguer et al. (2008), Ramos & Silva (2018) and Ottaviano et al. (2017) also observed that the H_2 production was dominated by butyric and acetic acids metabolic paths.

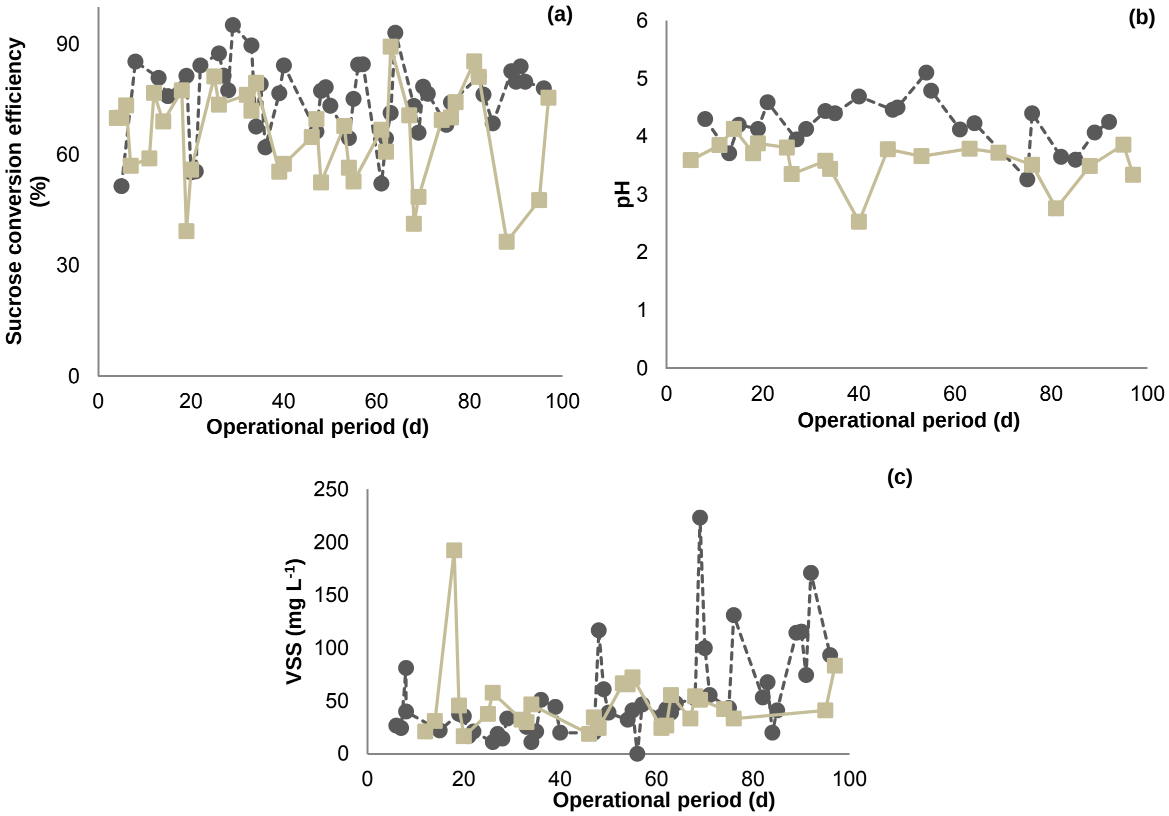

Figure 3 Overal performance of the reactors in the assayws: (a) sacarose convertion; (b) pH variation on the effluent and (c) SSV concentration in the effluent. Note: E1 (--●--) and E2 (—■—)

4. Conclusions

The CMTR presented stability in H_2 production, which allowed the production maintenance for long operational periods. The as worm thread made in the inner walls of the tube improved the performance of thesystem, which indicates that the biomass retention was sufficient to attend the conditions of the system. Therefore, this study points the technical viability of continuous hydrogen production in a continuous multiple tube reactor under mesophilic conditions. The main metabolic products were acetic and butyric acids.

Acknowledgments

The authors are grateful to the Coordination for the Improvement of Higher Level Personnel – Brazil (CAPES) and National Council for Scientific and Technological Development (CNPq, grant number 311741/2018-5) for supporting the development of this study.

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