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ARTIGO ORIGINAL

Two phases fermentative process for hydrogen and methane production from cassava wastewater

Processo fermentativo em duas fases para a produção de hidrogênio e metano a partir da manipueira

Aryane Mota Oliveira[1], Norma Candida dos Santos Amorim[1,2], Eduardo Lucena Cavalcante de Amorim[3] (orcid:0000-0002-7349-9055), Karina Ribeiro Salomon[4]

1. Doutoranda em Engenharia Civil pela Universidade Federal de Pernambuco (UFPE), Recife, PE, Brasil. 2. Docente do Instituto Federal de Alagoas (IFAL), Satuba, AL. 3. Docente do Programa de Pós-graduação em Engenharia Química do Centro de Tecnologia da Universidade Federal de Alagoas (UFAL), Maceió, AL, Brasil. 4. Docente da Universidade Federal de Alagoas (UFAL), Maceió, AL, Brasil.

Abstract

Introduction: Hydrogen and methane production was investigated in two phases of fermentative process. **Objective**: At the acidogenic phase, an anaerobic fluidized bed reactor was fed with cassava wastewater producing hydrogen. **Methods**: Expanded clay was used as a support material for biomass immobilization. The reactor was operated with HRT ranging from 8-1 h. **Results:** The best hydrogen yield production was 1.91 mol H2/mol glucose at HRT of 2 h. At the methanogenic phase, the acidogenic process effluent fed a fixed-bed reactor producing methane. **Conclusion**: Sururu (*Mytella falcata*) shells was used as support acted as pH neutralizer in the fixed-bed reactor, yielding best (0.430±0.150 $L_{methane}$/gCOD) with 12h HRT phase.

Key words: Anaerobic fluidized bed reactor. Biohydrogen. Biomethane. Dark fermentation. Cassava.

Resumo

Introdução: A produção de hidrogênio e metano foi avaliada em um processo fermentativo de duas fases. **Objetivo**: Na fase acidogênica, um reator anaeróbio de leito fluidificado foi alimentado com manipueira para a produção de hidrogênio. **Métodos**: Argila expandida foi utilizada com material suporte para a adesão microbiana. O reator foi operado com TDH, variando entre 8-1h. **Resultados**: O melhor rendimento de produção de hidrogênio foi 1.91 mol, H2/mol glicose em TDH de 2 h. Na fase metanogênica, o efluente do processo acidogênico alimentou um reator de leito fixo para a produção de metano. **Conclusão**: Conchas de Sururo (*Mytella falcata*) foram utilizadas como suporte, atuando como neutralizador do pH no reator de leito fixo, melhor rendimento (0.430±0.150 Lmethane/gDQO) na fase com TDH de 12h.

Palavras-chave: Reator anaeróbio de leito fluidificado. Bio-hidrogênio. Biometano. Fermentação. Mandioca.

INTRODUCTION

The fermentative biological process is a means to produce hydrogen sustainably, since it can make use of various types of carbohydrate-rich industrial and domestic waste as substrate, thereby mitigating problems caused by inappropriate disposal of this material. For that reason, the use of agro-industrial residues in biological hydrogen production has also been investigated[1,2].

Apparently, fermentative hydrogen production (acidogenesis) process does not significantly reduce the organic content of the feed. Usually, chemical oxygen demand (COD) removal is below 20% during hydrogen production process, which corresponds to a mean hydrogen production of 2.5 mol/mol glucose. This can be removed in a subsequent anaerobic digestion step with the conversion of organic content to methane[3].

Two-stage systems are preferred for anaerobic wastewater treatment as they are more stable than single stage systems[4]. In the first stage, organic matter is hydrolyzed and fermented to produce organic acids and hydrogen gas, while in the second stage organic acids are converted to methane by methanogens[5].

Most studies of co-digestion focused on the performance of single hydrogen production or single methane production, and limited information is available on the performance of co-digestion for hydrogen and methane production in two phase anaerobic system[6].

Hydrogen production by fermentative bacteria is highly dependent on the conditions of the process, such as pH, hydraulic retention time (HRT) and gas partial pressure, which affect the microbial metabolic balance and subsequently the fermentation end-products. In general, the dominant metabolism in a mixed acidogenic culture depends strongly on the pH of the microbial culture[7] and hydrogen production is suppressed by both low and high pH[8,9]. It has been reported that maximum hydrogen yields are obtained when the pH of the culture medium is between 5 and 6[7, 10], while the slower

Correspondência: Eduardo Lucena Cavalcante de Amorim. Federal University of Alagoas. Av. Lourival Melo Mota, s/n – Cidade Universitária – CEP 57072-900 – Maceió/AL – Brazil. E-mail: eduardo.lucena@ctec.ufal.br
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growing methanogenic bacteria stage, requiring a more neutral pH, were preferentially cultured in the second stage with a much longer hydraulic residence time[11].

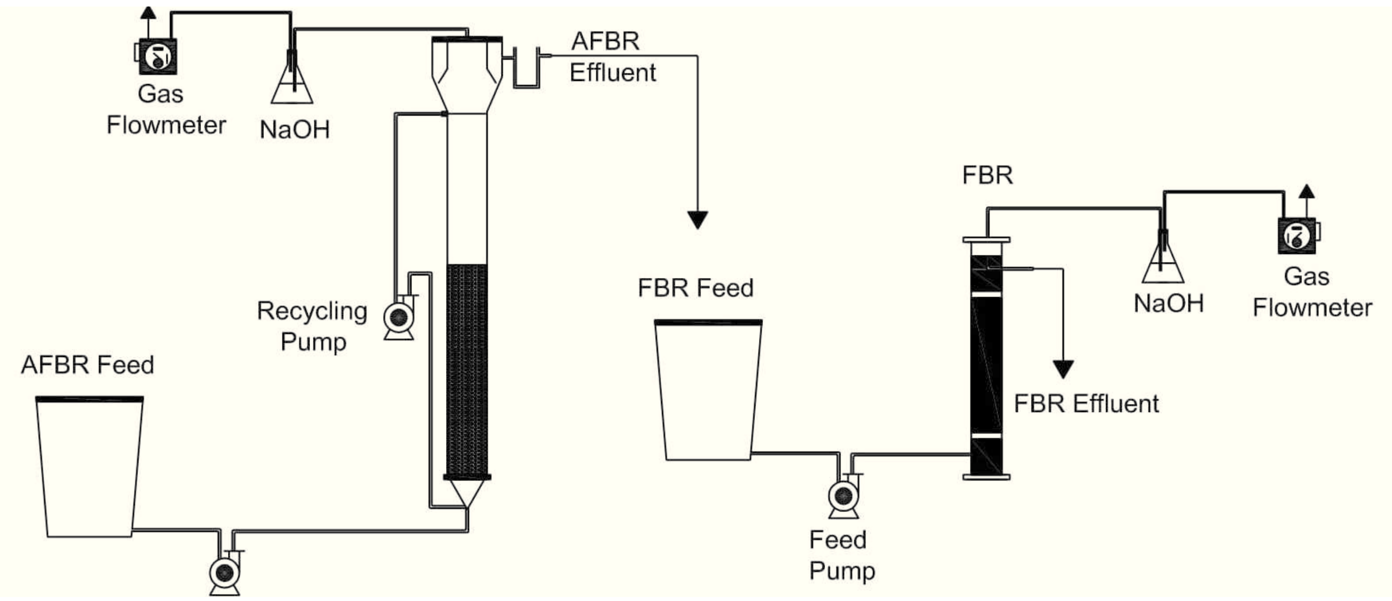
This study aims to assess the possibility of producing hydrogen from cassava wastewater with subsequent methane generation from its acidogenic process effluent via an anaerobic fluidized bed reactor (AFBR) and a fixed-bed reactor (FBR), respectively. At a methanogenic phase, Sururu (Mytella falcata) shells were used how pH neutralizer in this study.

Experimental

Cassava wastewater was obtained from a manioc flour factory in Taquarana, Alagoas, Brazil, with the following main characteristics: pH 5.53, total solids 4.45 g/L, volatile solids 3.4 g/L, total carbohydrate 37.54 g/L, chemical oxygen demand (COD) 66.19 g COD/L, total nitrogen 1.26 g/L.

Figure 1 shows a schematic of the two phases fermentative process system used in this study.

Figure 1: Schematic of the AFBR and FBR.



AFBR main body had a total volume of 4,192 cm^3, with its support material (1,065 g of expanded clay) static bed height of 90 cm[12].

AFBR was fed with cassava wastewater with 4,000 mgCOD/L. During the experiment the HRT decreased progressively from 8 to 1 h. Reactor was operated for 164 days. Operation temperature was not controlled (28 ± 2ºC) and reactor effluent pH was about 5.00±0.48. A gas–liquid separator was used at the effluent outlet to collect gaseous and soluble products separately. A gas meter (Type TG1; Ritter Inc., Germany) was used to measure the amount of gaseous products generated[12].

Cassava wastewater used in the FBR was AFBR effluent. FBR was operated in methanogenic phase and had sururu (Mytella falcata) shells as support material. The inoculum was obtained from a facultative sludge pond derived from swine wastewaters treatment. FBR bulk was 3,800 cm^3. Reactor was operated for 119 days, supplemented with alkalinity (1.25 g sodium bicarbonate/L) and yeast extract (0.5 g/L) until the 57th day of operation.

FBR operation was initially in a batch mode for 72h to active methanogenic biomass, being continuously operated soon after with 36h HRT, reduced sequentially to 24h and 12h.

In both reactors the following parameters were analyzed: COD, pH, volatile solids, total solids, fixed solids, total carbohydrate, volatile fatty acids and alkalinity.

Statistical analysis

The results were tested for homoscedasticity to determine whether the variances were equal (Shapiro-Wilk and Kolmogorov-Smirnov tests). Mann-Whitney tests (non-parametric) were used for variance analysis and for comparisons of averages, with 5% set as the significance level, as proposed by Dagnelie [13].

RESULTS AND DISCUSSION

Effect of HRT on hydrogen and methane production

Figure 2A shows hydrogen production rate (HPR) and hydrogen yield (HY) as functions of the hydraulic retention time (HRT). Figure 2B shows volumetric methane production (VMP) and its yield (MY) related to HRT.

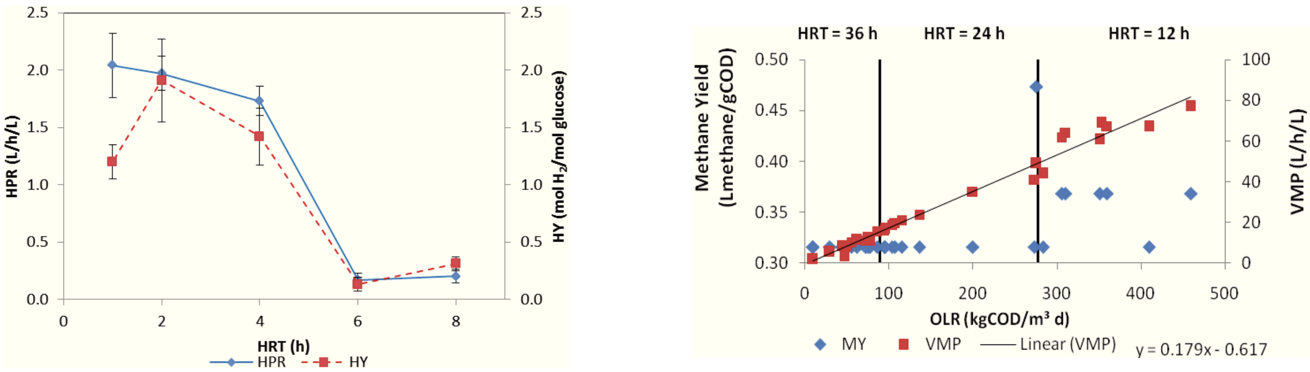
At AFBR, this study showed, according to Figure 2A, an increase in HPR from 0.20 to 2.04 L/h/L when decreasing the HRT from 8-1h, respectively. An increase in HY was observed when HRT decreasing from 8 (0.31 mol H2/mol glucose) to 2 hours (1.91 mol H2/mol glucose). A decrease in HY was subsequently observed when HRT decreased to 1 h (1.20 mol H2/mol glucose). This finding was also observed in previous studies employing an AFBR[12,14,15], and such behavior may be attributed to overloads caused by high organic loading rate (OLR) or kinetic limitations[12].

It is noted in Figure 2B that VMP grows with OLR, while MY remains constant for 36h and 24h HRTs, with a sudden growth at 12h HRT. Average MY values were 0.316±0.000 L/g, 0.338±0.060 L/g and 0.430±0.150 L/g, while VMP average values were 11.010±15.688 L/h/L, 42.463±24.824 L/h/L and 61.898±3.508 L/h/L for 36h, 24h and 12h HRTs, respectively; We concluded that 12h HRT was the most efficient.

A Tukey test with a significance level of 5% was used because the variables presented a normal distribution (for hydrogen production rate, HY and MY). The test indicated differences between the groups, which implies that the best conditions for hydrogen production, HY and MY were an HRT of 2 h and 12 h, respectively.

A Mann-Whitney test with a significance level of 5% was used for the variable with a non-normal distribution (HPR and VMP), and the test indicated that the values for the HPR and VMP were statistically different.

Figure 2. a) HPR and HY as functions of HRT at AFBR; b) VMP and MY related to OLR at FBR



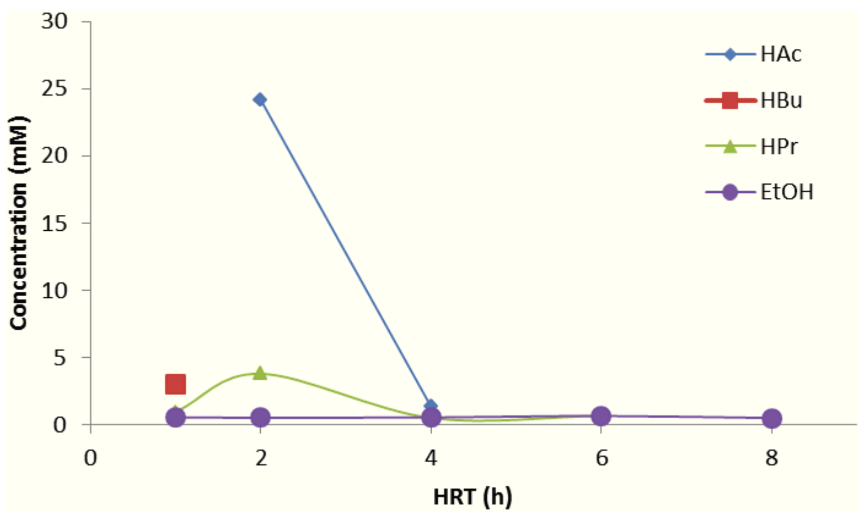
(a) (b)

Composition of soluble products at AFBR

Figure 3 shows the distribution of soluble microbial products (SMP) as a function of HRT at AFBR.

Ethanol was the most common metabolite during reactor operation, with its concentration ranging between 23.57 mg/L (0.51 mM) and 30.46 mg/L (0.66 mM) when the HRT was reduced from 8 to 6 h, and it presented an average production of 25.87 mg/L (0.56 mM), indicating an insignificant change in the production of this metabolite throughout AFBR operation. Propionic acid was the second most common metabolite during the experiment. The highest production of propionic acid was observed at an HRT of 2 h (280.98 mg/L or 3.8 mM). However, this production level did not prevent hydrogen production, which also increased at an HRT of 2 h. This result may be attributed to the high production of acetic acid at this HRT (1450 mg/L or 24.17 mM).

Figure 3: Effect of HRT on the performance of the AFBR. Soluble metabolites: (♦) HAc: acetate; (■) HBu: butyrate; (▲) HPr: propionate; (●) EtOH: ethanol



Acetic acid production was also observed at an HRT 4 h (80.0 mg/L or 1.33 mM). Compared to the previous phase, the pH increased from 4.72 (HRT of 6 h) to 5.56 (HRT of 4 h), which may have created the necessary conditions for the initiation of acetic acid production (1.33 mM). In addition, there was a small reduction in the production of propionic acid (0.51 mm at HRT of 4 h) compared to that of the previous phase (0.67 mM at HRT of 6 h), thereby indicating possible competition between these two metabolic pathways.

In contrast, acetic acid production was not observed at HRTs of 1 h, 6 h, and 8 h.

When the HRT was decreasing from 2 to 1 h, the acetic acid metabolic pathway was replaced with the butyric acid pathway. The butyric acid production at HRT of 1 h was 267.71 mg/L (3.04 mM).

Effect of Sururu shells as pH neutralizer in the FBR

Sururu shells acted as pH neutralizer in fixed-bed reactor, by losing calcium carbonate for the substratum, while losing mass. pH ranged from 7.01 to 8.48 in the methanogenic phase, ie, close to the ideal pH to methane production (between 6 and 8). pH below 6.5 or above 8.3 may decrease the rate of methane production [16].

The best VMP (61.898±3.508 L/h/L) and MY (0.430±0.150 L/g) was in the 12h HRT when the pH ranged from 7.19 to 7.91, within the range identified as optimal for methane production (6.5-8.3) [16]. At 36 h and 24 h HRT, the pH ranged from 7.01 to 8.48 and 7.38 to 8.25, respectively.

CONCLUSIONS

The performance of a two-stage continuous fermentation process with combined H2 and CH4 reactors using cassava wastewater was evaluated.

At AFBR, both the HPR and the HY significantly increased when the HRT was decreased, as shown by the maximum values of 2.04 L/h/L (HRT of 1 h) and 1.91 mol H2/mol glucose (HRT of 2 h), respectively.

The soluble metabolites present during the operation of the AFBR were acetic acid, butyric acid, propionic acid and ethanol. The predominance of propionic acid during the 8 h HRT (early phase of operations) was reflected in the low hydrogen production at this stage. This finding can be attributed to the adaptation phase of the reactor.

The high acetic acid production at HRT of 2 h coincides with the largest HY, which may be attributed to the greater deflection of the electron flow route for acetic acid production at this stage.
At FBR, the sururu shells were efficient as pH neutralizer. The MY showed better values at HRT of 12 h (0.430±0.150 Lmethane/gCOD), while was observed the increasing of VMP when the HRT decreased from 36 to 12 h (11.010 - 42.463 L/h/L).

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REFERÊNCIAS

1. Luo G, Xie L, Zou Z,Wang W, Zhou Q. Exploring optimal conditions for thermophilic fermentative hydrogen production from cassava stillage. Int J Hydrogen Energy. 2010 Jun; 35(12): 6161-6169. doi: http://dx.doi.org/10.1016/j.ijhydene.2010.03.126.

2. Wu SY, Lin CN, Chang JS. Hydrogen production with immobilized sewage sludge in three-phase fluidized-bed bioreactor. Biotechnol Prog. 2003 May-Jun; 19(3): 828-832. doi: 10.1021/bp0201354.

3. Antonopoulou G, Gavala HN, Skiadas IV, Angelopoulos K, Lyberatos G. Biofuels generation from sweet sorghum: Fermenttive hydrogen production and anaerobic digestion of the remaining biomass. Bioresour Technol. 2007 Jan; 99(1): 110-119. doi: 10.1016/j.biortech.2006.11.048.

4. Viéitez ER, Ghosh S. Biogasification of solid wastes by two-phase anaerobic fermentation. Biomass Bioenergy. 1999 May; 16(5): 299–309. http://dx.doi.org/10.1016/S0961-9534(99)00002-1.

5. Ginkel SWV, Logan BE, Oh SE. Biohydrogen gas production from food processing and domestic wastewater. Int J Hydrogen Energy. 2005 Dec; 30(15): 1535-1542. doi: 10.1016/j.ijhydene.2004.09.017.

6. Wang W, Xie L, Chen J, Lou G, Zhou Q. Biohydrogen and methane production by co-digestion of cassava stillage and excess sludge under thermophilic conditions. Bioresour Technol. 2011 Feb; 102(4): 3833-3839. doi: 10.1016/j.biortech.2010.12.012.

7. Lay JJ. Modelling a nd optimization of anaerobic digested sludge converting starch to hydrogen, Biotechnol. Bioeng, 2000 May; 68(3): 269–278. PubMed PMID: 10745195.

8. Ueno Y, Otsuka S, Morimoto M. Hydrogen production from industrial wastewater by anaerobic microflora in chemostat culture. Journal of Fermentation and bioengineering. 1996; 82(2): 194-197. doi: http://dx.doi.org/10.1016/0922-338X(96)85050-1.

9. Chen CC, Lin CY, Lin MC. Acid-base enrichment enhances anaerobic hydrogen production process. Appl. Microbiol. Biotechnol. 2002; 58: 224-228. doi:10.1007/s002530100814.

10. Fang HHP, Liu H. Effect of pH on hydrogen production from glucose by a mixed culture. Bioresour Technol. 2002 March; 82(1): 87-93. doi: http://dx.doi.org/10.1016/S0960-8524(01)00110-9.

11. M. Cooney, N. Maynard, C. Cannizzaro, J. Benemann. Two phase anaerobic digestion for production of hydrogen-mathane mixtures. Bioresour Technol. 2007 Oct; 98(14): 2641-2651. doi: 10.1016/j.biortech.2006.09.054.

12. Amorim ELC, Barros AR, Damianovic MHRZ, Silva EL. Anaerobic fluidized bed reactor with expanded clay as support for hydrogen production through dark fermentation of glucose. Int J Hydrogen Energy. 2009 Jan; 34(2): 783-790. doi: http://dx.doi.org/10.1016/j.ijhydene.2008.11.007.

13. Dagnelie P. Estatística: teoria e métodos II. Porto: Europa-América; 1973.

14. Barros AR, Amorim ELC, Reis CM, Shida GM, Silva EL. Biohydrogen

production in a anaerobic fluidized bed reactors: effect of support material and hydraulic retention time. Int J Hydrogen Energy. 2010 Apr; 35(8): 3379-3388. doi: http://dx.doi.org/10.1016/j.ijhydene.2010.01.108.

15. Reis CM, Silva EL. Effect of upflow velocity and hydraulic retention time in anaerobic fluidized-bed reactors used for hydrogen production. Chem Eng J. 2011 Aug; 172 (1): 28-36. doi: http://dx.doi.org/10.1016/j.cej.2011.05.009.

16. R. E. Speece. Anaerobic biotechnology for industrial wastewater treatment. Environ Sci Technol. 1983 Sep; 1;17(9):416A-27A. doi: 10.1021/es00115a725.

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