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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 2: Hydrogen Production Technologies – Part 1

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-2

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-652-1

# Effect of Alkalinity and Organic Loading Rate in the Fermentative H<sub>2</sub> Production from an Anaerobic Fluidized Bed Reactor

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## 1 Introduction

Currently, 90% of global energy is generated from fossil fuels. However, we now know that fossil fuel reserves are scarce, and their combustion generates various environmental problems. Replacing fossil fuels, which produce carbon dioxide as a combustion product, with hydrogen could be an alternative to ameliorate the greenhouse effect. Hydrogen is considered a clean fuel, generating water as a combustion product in electrolytic fuel cells, and it presents a high energy per unit mass (122 kJ g<sup>-1</sup>), which is 2.75-fold greater than that of hydrocarbon fuels (Das and Verziroglu, 2001 [1]).

Several biological processes have shown potential for the sustainable production of hydrogen and require low energy inputs; thus, they are considered to be promising alternatives to conventional physical/chemical production of H<sub>2</sub>. Hydrogen can be produced from biomass and/or a fraction of biodegradable waste, for use as a biofuel. Among the several alternatives of biological H<sub>2</sub> production, the use of an anaerobic fluidized-bed reactor (AFBR) has been shown to be efficient (Wu et al., 2006 [2]; Zhang et al., 2007 [3]). There are still several practical issues to be studied; among these are the conditions for optimized hydrogen production and limited growth of methanogens. These conditions include short hydraulic retention time (HRT), short cell retention time and low pH. Another method that can increase biological hydrogen production is thermal shock treatment of the inoculum, which removes spore-forming bacteria, some of which are consumers of hydrogen (Lay, 2001 [4], Van Ginkel et al., 2002 [5]). In previous studies (Van Ginkel et al., 2002 [5]), the heat treatment along with low pH were limiting factors for the growth of hydrogen-consuming microorganisms. Chen et al. (2005) [6] concluded that the optimum pH was 5.0 for hydrogen production. Fan and Chen (2004) [7] and Fang and Liu (2002) [8] obtained an optimum pH of 5.5. Khanal et al. (2004) [9] also obtained an optimum pH of 5.5 for hydrogen production; however, for volatile organic acid production (acetic and butyric acid), the optimum pH was between 3.0 and 4.0. However, Mu et al. (2006) [10] found the optimum pH for hydrogen production to be 4.2.

Due to this lack of consistent information on the optimum pH for hydrogen production, the stability of two identical anaerobic fluidized-bed reactors using expanded clay for microbial adhesion, R1, operated without pH control, and R2, operated with the addition of alkalinity to

control pH, were compared by varying the HRTs (organic loading rate) and evaluating their performances.

## 2 Material and Methods

### 2.1 Medium composition

The reactors were operated using a synthetic substrate containing glucose as the sole carbon source at a concentration of 2,000 mg L<sup>-1</sup> plus the following nutrients (mg L<sup>-1</sup>): CH<sub>4</sub>N<sub>2</sub>O, 125; NiSO<sub>4</sub>·6H<sub>2</sub>O, 1; FeSO<sub>4</sub>·7H<sub>2</sub>O, 5; FeCl<sub>3</sub>·6H<sub>2</sub>O, 0.5; CaCl<sub>2</sub>·6H<sub>2</sub>O, 47; CoCl<sub>2</sub>·2H<sub>2</sub>O, 0.08; SeO<sub>2</sub>, 0.07; KH<sub>2</sub>PO<sub>4</sub>, 85; KHPO<sub>4</sub>, 21.7; and Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O, 33.4. Reactor R1 was operated without pH control and R2 was operated with the addition of alkalinity (sodium bicarbonate 2,000 mg L<sup>-1</sup>) as needed to maintain a pH of 5.0-5.5.

### 2.2 H<sub>2</sub>-producing sludge and immobilization of H<sub>2</sub>-producing

The inoculum used was sludge from an upflow anaerobic-sludge blanket (UASB) reactor treating effluent from swine-manure wastewater. The sludge was subjected to heat-treatment in accordance with the methodology described by Kim et al. (2006) [11]. This heat treatment allowed for the removal of vegetative cells of methanogenic and acidogenic bacteria not capable of forming endospores, which are structures resistant to adverse conditions. Acidogenic cells capable of spore formation remained as a viable culture. The selection was performed as described in Maintinguier et al. (2008) [12]. Particles of expanded clay (2.8–3.35 mm) were used as a support material for biomass immobilization.

### 2.3 Analytical methods

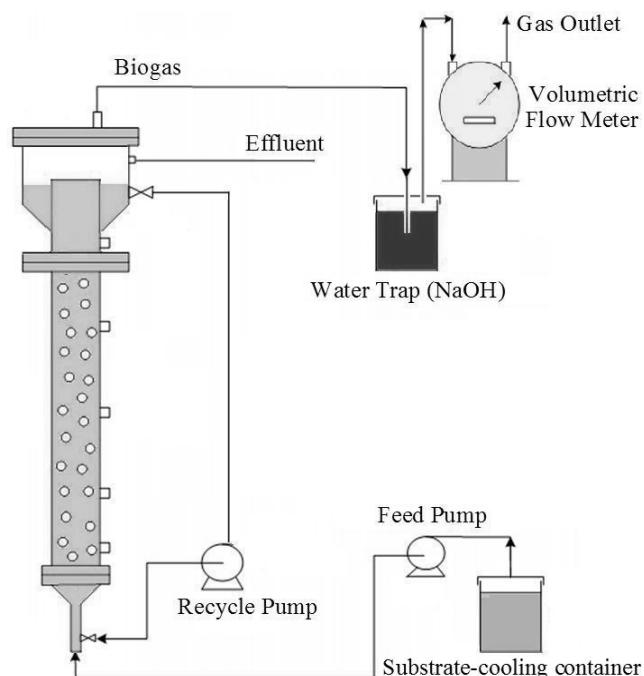
Hydrogen gas was identified with a gas chromatograph (GC-2010, Shimadzu, Tokyo, Japan) that was equipped with a thermal conductivity detector (TCD). The carrier gas was argon, and the column was packed with Supelco Carboxen 1010 Plot (30 m × 0.53 mm i.d.) (Maintinguier et al., 2008 [12]). The volatile fatty acid (VFA) and alcohol concentrations were measured using a gas chromatograph (GC-2010, Shimadzu, Tokyo, Japan) that was equipped with a flame-ionization detector (FID), a COMBI-PAL headspace autosampler (AOC model 5000) and an HP-INNOWAX column (30 m × 0.25 mm i.d. × 0.25 µm of film thickness) (Maintinguier et al., 2008 [12]). The pH and chemical oxygen demand (COD) were measured according to the procedures described in the Standard Methods (1998) [13]. The glucose concentrations of the reactor influent and effluent were determined by a method using an enzymatic reaction with glucose oxidase (Amorim et al., 2009 [14]).

### 2.4 Set-up and operation of AFBR for H<sub>2</sub> production

The experiments were carried out in two conventional anaerobic fluidized-bed reactors. The main body of the reactor was a vertical cylindrical column 5.3 cm in diameter and 190 cm in height. For the AFBR, the recycle rate was controlled at 128 L/min (bed expansion = 30%), which maintained good fluidization of the particles in the reactor. The bioreactor was initially operated in batch mode for 48 h to activate the H<sub>2</sub>-producing sludge before it was switched

to a continuous mode at a designated hydraulic retention time (HRT = 8 h, 6 h, 4 h, 2 h or 1 h). The schematic diagram of the experimental system is shown in Figure 1.

After reaching steady-state operation (based on a constant volumetric H<sub>2</sub>-production rate within a variation of 5-10% for 10-15 days), the HRT was decreased progressively from 8 h to 1 h. The compositions of the gaseous products (H<sub>2</sub> and CO<sub>2</sub>) and soluble metabolites (volatile fatty acids and alcohol) produced during H<sub>2</sub> fermentation were monitored as functions of time. The reactor was operated at a temperature of 30°C. Reactor R1 was operated at an effluent pH within 3.68-4.05. Reactor R2 was operated at an effluent pH within 5.09-5.54. A gas meter (Type TG1; Ritter Inc., Germany) was used to measure the amount of gaseous products generated.

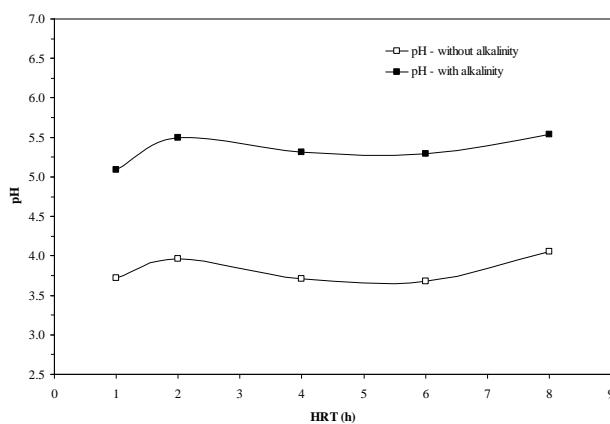


**Figure 1: Diagram of the anaerobic fluidized-bed reactor (AFBR).**

### 3 Results and Discussion

The effect of HRT on hydrogen production was evaluated as the reactors were operated without the addition of alkalinity (R1), with the addition of alkalinity (R2) and influent glucose concentration of 2,000 mg L<sup>-1</sup>.

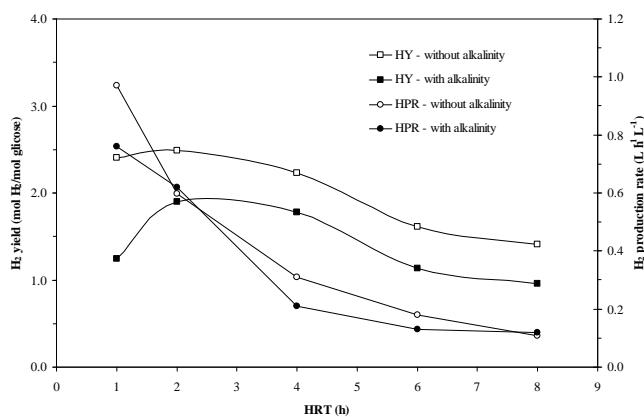
Figure 2 shows the pH behaviour resulting from the varying HRT applied to reactors. In the reactor without the addition of alkalinity (R1), the pH ranged from 3.68 to 4.05; for the reactor with the addition of alkalinity (R2), the pH ranged from 5.09 to 5.54.



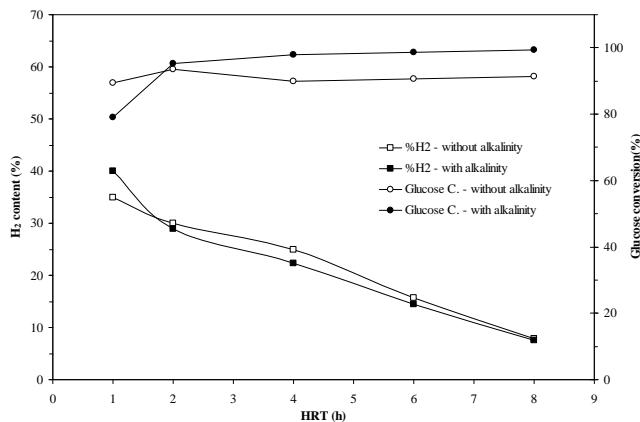
**Figure 2: Performance of effluent pH in the reactors: R1 (□) (without added alkalinity) and R2 (■) (with added alkalinity).**

As shown in Figure 3, the hydrogen-production rates (HPR) in reactors R1 and R2 increased from 0.08 to 0.97 L h<sup>-1</sup> L<sup>-1</sup> and from 0.12 to 0.76 L h<sup>-1</sup> L<sup>-1</sup>, respectively, by decreasing the HRT of 8 h to 1 h. For both reactors, the hydrogen-production rate increased slightly from an HRT of 8 h to 4 h but almost doubled at an HRT of 2 h compared to that at 4 h (Figure 3). A substantial increase was observed with an HRT of 1 h; this increase was related to the increased organic loading and growth of biomass. This finding indicates that the metabolic flux may have shifted during the transition of HRT from 8 h to 1 h, when most of the substrate was shifted to the reactions of end-products instead of bacterial growth and maintenance, resulting in increased hydrogen yield (Zhang et al., 2007 [3]). With a decrease of HRT from 8 h to 2 h, the hydrogen yield (HY) increased from 1.41 to 2.49 mol H<sub>2</sub>/mol glucose in R1 and from 0.96 to 1.90 mol H<sub>2</sub>/mol glucose in R2. However, when HRT was decreased to 1 h, the hydrogen yield in reactors R1 and R2 also decreased, to 2.41 and 1.24 mol H<sub>2</sub>/mol glucose, respectively. This decrease in HY during the transition of the HRT from 2 h to 1 h may be attributed to kinetic limitations caused by the increase in the organic-loading rate in the reactor.

The glucose conversion in reactors R1 and R2 varied between 89.5-93.6% or 79.0-99.3%, respectively (Figure 4). The H<sub>2</sub> content of the biogas in reactors R1 and R2 increased from 8% to 35% and from 8% to 40%, respectively, with the decrease in the HRT from 8 h to 1 h (Figure 4). Also using AFBRs, Wu et al. (2003) [2] and Lin et al. (2006) [15] obtained substrate conversions above 90% and between 92% and 99%, respectively, for HRTs of 8 h and 1 h. However, Zhang et al. (2007) [3] found that the glucose conversion decreased from 99.47% to 71.44% when the HRT was decreased from 4 h to 0.5 h.



**Figure 3:** Effect of HRT on the AFBR performance:  $H_2$  production rate and  $H_2$  yield production. (□) R1-HY and (■) R2-HY; (○) R1-HPR and (●) R2-HPR. HY:  $H_2$  yield ([mol of  $H_2$  formed]/[mol of glucose consumed]); HPR:  $H_2$ -production rate.



**Figure 4:** Effect of HRT on the performance of the reactors:  $H_2$  content and glucose conversion. (□) R1  $H_2$  content and (■) R2  $H_2$  content; (●) R2 glucose conversion and (○) R1 glucose conversion. Glucose conversion: (mol of glucose utilized)/(mol of glucose fed into the reactor).

Table 1 shows the behaviour of the levels of the main metabolites produced in reactors R1 and R2 during operation under different HRTs.

**Table 1: Composition of soluble metabolites under different HRTs in the AFBRs.**

HRT (h)	Reactor R1 (without pH control )				Reactor R2 (with pH control )			
	HAc (%)	HBu (%)	HPr (%)	EtOH (%)	HAc (%)	HBu (%)	HPr (%)	EtOH (%)
8	36.28	44.66	0.00	19.06	31.58	11.84	8.53	48.05
6	36.12	44.87	0.00	19.01	39.94	12.93	14.57	32.56
4	48.85	37.73	0.00	13.42	46.47	12.67	10.55	30.31
2	53.32	39.65	0.00	7.03	52.51	13.77	7.37	26.34
1	50.55	41.60	0.00	7.85	36.12	26.04	16.89	20.95

**HAc: acetate; HBu: butyrate; HPr: propionate; EtOH: ethanol.**

In the reactor without added alkalinity (R1), the products, in ascending order, were ethanol (7.03%-19.06%), acetate (36.12%-53.32%) and butyrate (37.73%-44.87%). Propionate was not detected during the entire operation of reactor R1. This should enhance the increase in hydrogen production in these reactors, as the biosynthetic route for the production of propionate results in the consumption of two moles of H<sub>2</sub> for every two moles of propionic acid produced (Eq. 1), and may be related to inhibition likely caused by low pH and sensitivity to short HRT, as has been reported by other researchers (Zhang et al., 2007) [3].



In the reactor with alkalinity addition (R2), the products in ascending order were propionate (7.37%-16.89%), butyrate (11.84%-26.04%), ethanol (20.95%-48.05%) and acetate (31.58-52.51%).

#### 4 Conclusion

The hydrogen production rate, hydrogen yield and H<sub>2</sub> content all increased with the reduction of HRT from 8 h to 1 h. The reactor without added alkalinity (R1) showed higher hydrogen production rates and hydrogen yields at all HRTs evaluated, although the H<sub>2</sub> content as a percentage of the biogas was similar in both reactors. The reactor R1 did not produce propionic acid, resulting in a higher hydrogen yield. These results indicate that both conditions (with or without the addition of alkalinity) are suitable for hydrogen production; however, the production in the reactor without added alkalinity was higher at all stages, and therefore that setup is the better option for hydrogen production in an anaerobic fluidized-bed reactor.

#### Acknowledgement

The authors gratefully acknowledge the financial support of CNPq and FAPESP.

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