WASTE-TO-ENERGY USING A NOVEL INTEGRATED BIOLOGICAL PROCESS

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ABSTRACT

This study compared the performance of a novel technology for biological hydrogen production from glucose and corn-syrup with the performance of the conventional continuously stirred tank reactors (CSTR). The novel technology, termed biohydrogenator (patent-pending), comprises CSTR with gravity settlers to decouple hydraulic retention time (HRT) from solids retention time (SRT). Two biohydrogenators and two CSTR systems were operated at organic loading rates of 6.5-42.8 gCOD/L/d, and HRTs of 8-12 hours. The SRT was maintained at 2 days in the two biohydrogenators. The decoupling of SRT from HRT not only increased glucose conversion to volatile fatty acids and hydrogen from 29-50% in the CSTR to 99.9% in the biohydrogenators, but also the volumetric hydrogen production from 0.55-1.8 in the CSTRs to 2.4-9.6 L/L/d. Hydrogen yield increased from 0.5-1.0 mol H_2/mol glucose converted in the CSTR to 2.8 mol H_2 /mol glucose converted in the biohydrogenators. DGGE analysis confirmed the specificity of the microbial culture in the biohydrogenators with the high hydrogen producing *Clostridium* species, as compared to the more diverse cultures in the CSTR. The biohydrogenator was then tested on a corn-syrup waste generated as a by-product from an industrial facility for bioethanol production located in South Western Ontario, Canada. Glucose was the main constituent in the corn-syrup; its concentration was varied over a period of 90 days from 8 to 25 g/L. The change in glucose concentration was used to study the impact of variable organic loading on the stability of hydrogen production in the biohydrogenator. Hydrogen production rate increased from 10 L H_2 /L /d to 34 L H_2 /L /d with the increase of organic loading rate (OLR) from 26 to 81 gCOD/L/d, while a maximum hydrogen yield of 430 L H_2 / kgCOD was observed.

Keywords: Biological hydrogen production, CSTR, Gravity settler, Corn-syrup

1. INTRODUCTION

Hydrogen does not contribute to the greenhouse effect and has a high energy yield of 142 kJ/g, 2.75 times more than that of any hydrocarbon [1]. Biological hydrogen production is regarded as one of the most promising alternatives for sustainable green energy production, notwithstanding the feasibility of hydrogen production through water electrophoresis and chemical cracking of hydrocarbons. Among different biological processes for hydrogen production, dark fermentation is the most attractive one because of its potential of direct use of wastewater streams and organic wastes and its higher rate of hydrogen production in comparison with photo-fermentative processes.

The conversion of organic waste into hydrogen is attractive both from pollution control and energy recovery points of view. However, only a few studies have been conducted for hydrogen production from real wastewater due to challenges associated with inhibition and microbial shifts. Table 1 shows the process conditions and system performances of selected literature studies using wastewaters from rice winery [2], noodle [3], sugar [4], [5], sugar beet [6] and molasses manufacturing [7], food processing [8], and filtered leachate of municipal solid wastes [9]. The highest hydrogen yield of 321 L H_2/kgCOD was demonstrated by Ueno et al. [4] for the treatment of sugar factory wastewater in a continuous stirred tank reactor (CSTR) with 63% glucose conversion efficiency. With the exception of the two batch studies with soil microorganisms as seed [7] and [8], most of the studies achieved around 200 L H_2/kgCOD. Furthermore, as shown in Table 1, packed bed reactors (PBR) have no advantage over continuously stirred tank reactors (CSTR) in terms of hydrogen production.

The maximum specific growth rate (μ_{max}) for mixed cultures of hydrogen producing bacteria of 0.333 h^{-1} [10] corresponds to a minimum solids retention time (SRT_{min}) of 3.0 h and thus CSTRs operated for hydrogen production are characterized by hydraulic retention time (HRT) of 3-8 h. However, high dilution rates result in a marked decrease in biomass content in the reactor due to severe cell washout and system failure ensues [11]. Although, fill and draw (fed-batch) reactors have been used for hydrogen production, they invariably suffered from inconsistent hydrogen production [12] and methane production [13].

In order to overcome biomass washout in hydrogen reactors, decoupling of SRT from HRT in hydrogen bioreactors has been achieved primarily by using biofilms on several media including synthetic plastic media and treated anaerobic granular sludge [14], activated carbon, expanded clay and loofah sponge [15], glass beads [16] and membranes [17]. Problems with the development of methanogenic biofilms on the carrier media adversely impact process stability, which is critical for sustained hydrogen production. Moreover, membranes have not shown many advantages in terms of volumetric hydrogen yield and are also prone to fouling in such a reductive environment. Thus, this innovative research will involve a side by side comparison between the conventional biohydrogen continuously stirred tank reactors and the novel biohydrogenator, and hydrogen production from real waste will be assessed. Moreover, the paper will focus on the performance of the biohydrogenator under variable organic loadings, highlighting the various mechanisms contributing to hydrogen production.

Table 1. Process and Performance Parameters for Actual Wastewaters

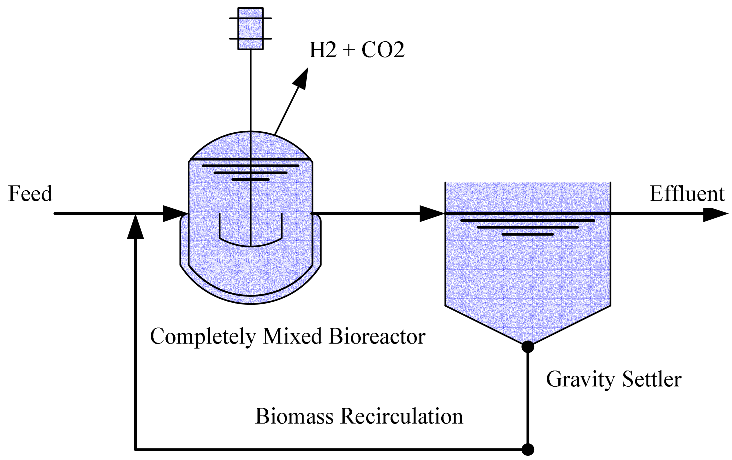
Feedstock	Reactor type	Seed sludge	pH	Temperature (°C)	HRT (h)	Hydrogen Content (%)	Yield (L H_2/ kgCOD)	Maximum volumetric rate (L H_2/L/d)	Ref.
Sugar factory wastewater	CSTR	Compost	6.8	60	12	64	321	4.8	[4]
Wastewater containing sugar and ethyl alcohol	PBR	ADS	6.0-6.5	37	8	60	-	1.8	[5]
Molasses	Batch	Soil	6.0	26	-	-	102	-	[7]
Noodle manufacturing wastewater	CSTR	ADS	5.2	35	18	-	187	-	[3]
Rice winery wastewater	PBR	AS	5.5	55	2	61	272	3.8	[2]
Filtered leachate of waste biosolids	Batch	Waste biosolids	6.7-6.9	35	-	-	184	-	[9]
Sugar beet wastewater	CSTR	ADS	5.2	32	15	57	216	3.0	[6]
Food processing wastewater	Batch	Soil	4.0-6.4	23	-	60	100	3	[8]

Note. CSTR, continuous stirred tank reactor; PBR, packed-bed reactor; ADS, anaerobic digested sludge; AS, acclimated sludge

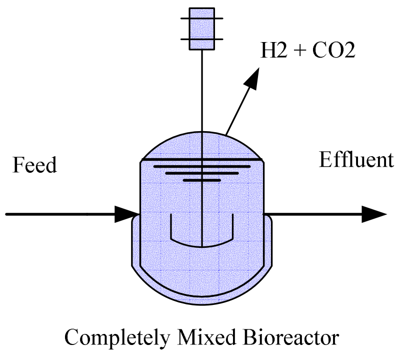
MATERIALS AND METHODS

Systems set up and operations

Part 1: Four lab-scale systems (Figure 1) were operated at 37°C for 65 days. Two integrated biohydrogen reactor clarifier systems (Biohydrogenators) (1 and 2) [18], denoted henceforth as IBRCS-1 and IBRCS-2, comprised a continuously stirred reactor (CSTR) for biological hydrogen production (5 L working volume), followed by uncovered gravity settler (volume 8 L) i.e. open to atmosphere, while CSTR-1 and 2 consisted of a CSTR only with a working volumes of 5 L and 2 L, respectively. Details of the operational conditions for the four systems are listed in Table 2.



a) Biohydrogenator



b) CSTR

Figure 1. Experimental Setup for the biohydrogen production systems

Table 2. Operational conditions in the hydrogen producing systems

	Glucose (g/L)	HRT (h)	SRT (h)	OLR (gCOD/L/d)	pH
IBRCS -1	2	8	48 ± 3.2	6.5	5.5-6.5
IBRCS -2	8	8	46 ± 4.2	25.7	5.5-6.5
CSTR-1	8	8	8	25.7	5.5-6.5
CSTR-2	20	12	12	42.8	5.5 (controlled)

Part 2: The biohydrogenator was then operated for 100 days at 37°C on corn-syrup waste. The system was seeded with 5 litres of sludge and started up in a continuous mode with the feed containing 8 g/L glucose. Solids retention time was controlled by sludge wastage from the clarifier. The feed contained sufficient inorganics (mg/L): $NaHCO_3$, 4000; $CaCl_2$, 140; $MgCl_2.6H_2O$, 160; NH_4HCO_3, 600; $MgSO_4.7H_2O$, 160; urea, 500; Na_2CO_3, 124; $KHCO_3$, 156; K_2HPO_4, 15; trace mineral solution, 500; H_3PO_4, 250. After 10 days, when the system reached steady state, the feed was

switched to corn-syrup waste generated as a by-product from an industrial facility for bioethanol production located in South Western Ontario, Canada. The corn-syrup was characterized by total suspended solids (TSS) of 400-500 g/L; soluble chemical oxygen demand (SCOD) of 100-350 g/L; glucose of 80-300 g/L and a pH of 3.5-4.5.

The experimental period consisted of three consecutive phases of 30 days each. The waste was diluted with tap water to approximately 1:10 according to the desired OLR for each phase of the experiment. The organic loading rate was increased in a stepwise fashion from 26 gCOD/L/d in Phase 1 to 52 and 81 gCOD/L/d in Phases 2 and 3, respectively. Based on the influent flow rate of 15 L/d, the bioreactor HRT was maintained constant at 8 hours in all three phases of operation while the SRT varied narrowly from 2.2 to 2.5 days due to variations in system effluent VSS. The SRT was estimated according to the amount of VSS (g) in the hydrogen bioreactor (excluding biomass in the clarifier) divided by the summation of the amount of VSS (g/d) leaving the system in both the clarifier liquid effluent and waste sludge.

Inocula and media compositions

Anaerobicaly-digested sludge from the St. Mary's wastewater treatment plant (St.Mary, Ontario, Canada) was used as the seed. In order to enrich hydrogen producing bacteria, the seed sludge was heat treated at 70 °C for 30 minutes.

Analytical Methods

The biogas composition including hydrogen , methane and nitrogen was determined by a gas chromatograph (Model 310, SRI Instruments, Torrance, CA) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (Molesieve 5A, mesh 80/100, 6 ft X 1/8 in). Argon was used as carrier gas at a flow rate of 30 mL/min. The temperatures of the column and the TCD were 90 and 105 °C, respectively. The concentrations of volatile fatty acids (VFAs) were analyzed using a gas chromatograph (Varian 8500, Varian Inc., Toronto, Canada) with a flame ionization detector (FID) equipped with a fused silica column (30m × 0.32 mm). Helium was used as carrier gas at a flow rate of 5 mL/min. The temperatures of the column and detector were 110 and 250 °C, respectively. Lactic acid concentrations were measured using a high-performance liquid chromatography system (1200 series, Agilent Technologies) equipped with Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm I.D.; BIO-RAD), and a UV-detector at 210 nm. The column temperature was adjusted to 30 °C. The same instrument with a refractive index detector (RID) was used to measure the concentrations of glucose. The temperature of the RID detector was set to 35 °C. The amount of volatile suspended solids (VSS) and chemical oxygen demand (COD) were measured according to standard methods [19].

RESULTS AND DISCUSSIONS

Part 1: Figures 2 a and b show the hydrogen production rate and yield profiles, respectively, for the four reactors throughout the 65 days of operations. All the reactors showed stable hydrogen production during the two months of operation. However, the coefficient of variation (calculated as standard deviation divided by the average) for hydrogen production rate in CSTR-2 was 20% in comparison with approximately 10% variation in other reactors. IBRCS-2 showed a drastically higher hydrogen production rate than other systems. Comparing IBRCS-2 and CSTR-1, which were operated at same OLR, hydrogen production rate in IBRCS-2 gradually increased during the first 10 days of operation from 5.5 L/L/d to 11 L/L/d; while in CSTR-1 hydrogen production decreased during the first ten days of operation and stabilized at 1.8 L/L/d. However, in the CSTR with higher organic loading rate (CSTR-2) hydrogen production rate dropped to approximately 0.6 L/L/d after 7 days. Comparing IBRCS-1 and IBRCS-2 (see Table 3) under two different OLRs (6.5 and 25.7 gCOD/L/d), respectively, the hydrogen yield was the same in both systems during steady state operation. The average hydrogen production rates in IBRCS-1 and IBRCS-2 were 2.4 L/L/d and 9.6 L/L/d, respectively.

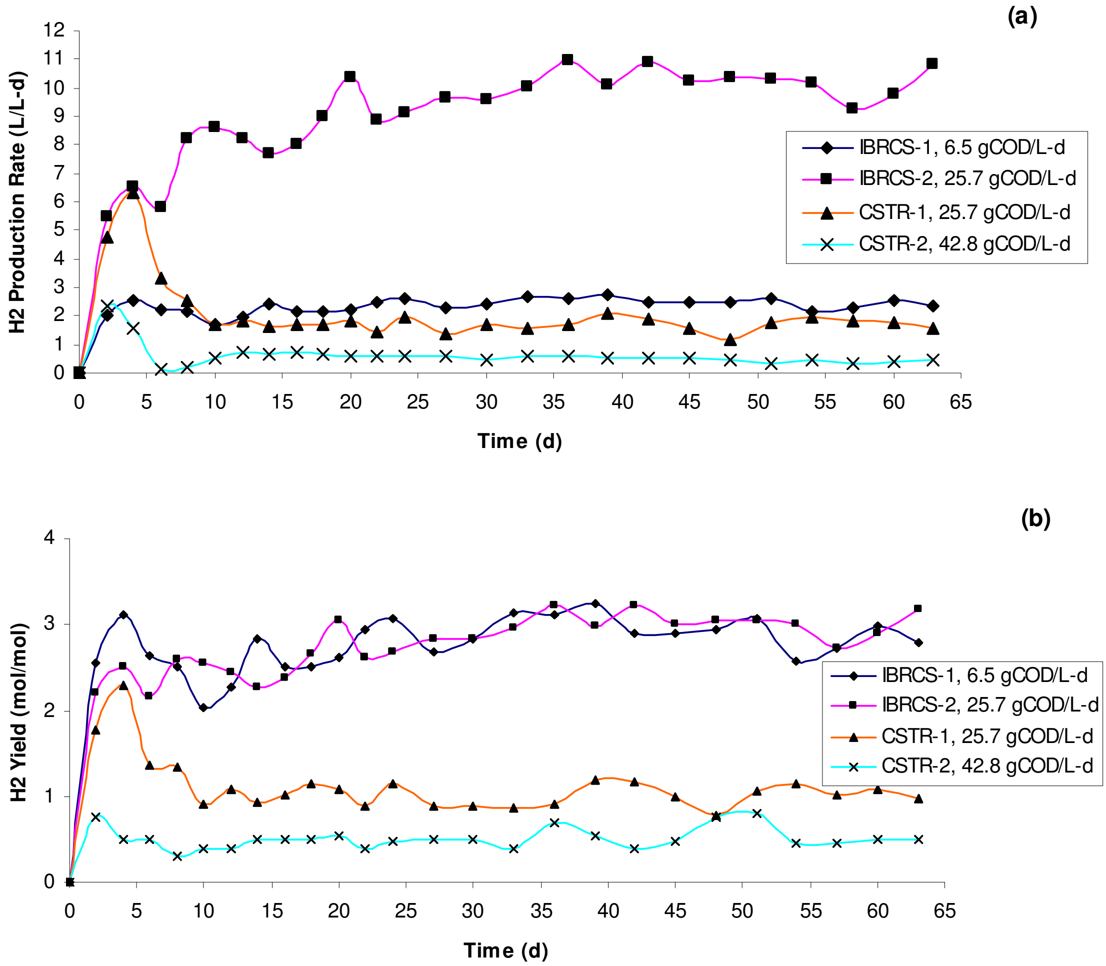


Figure 2. Diurnal variation in: a) hydrogen production rate, b) hydrogen yield

Table 3. Summary of steady state data in the hydrogen production systems

	Hydrogen Gas (%)	Hydrogen Gas (L/L/d)	Hydrogen Yield (mol/mol)	% Glucose converted	Biomass Yield (gVSS/gglucose)
IBRCS -1	71 ± 0.9	2.4 ± 0.2	2.8 ± 0.3	99.9 ± 0.1	0.12 ± 0.02
IBRCS -2	73 ± 2.7	9.6 ± 0.9	2.8 ± 0.3	99.9 ± 0.1	0.09 ± 0.01
CSTR-1	66 ± 5.3	1.8 ± 0.2	1.0 ± 0.1	50 ± 3.5	0.19 ± 0.02
CSTR-2	76 ± 3.6	0.55 ± 0.11	0.5 ± 0.1	29 ± 5.7	0.29 ± 0.02

Note. Values represent average ± standard deviation

In order to validate the experimental results, a numerical modeling comparison between the biohydrogenator and the conventional CSTRs was performed using the commercial software Biowin (Envirosim Associates, Burlington, Ontario, Canada). As apparent from Table 4, at the same range of the operational glucose concentrations, the model well predicted all the key parameters for the biohydrogenator as well as the CSTR. The comparison between biomass concentrations and hydrogen production rates in both the biohydrogenator and the CSTR, have revealed that indeed there was a severe washout in biomass concentrations in the conventional CSTR that lead into a marked decrease in the hydrogen production rates. The hydrogen production rate in the biohydrogenator ranged from 2.5-40 L/L/d compared to 0.5-10.7 L/L/d in the CSTR with the increase in the glucose concentrations from 2g/L to 32 g/L.

Table 4. Numerical modeling comparing IBRCS and CSTRs different glucose concentrations

	2 g glucose/L		8 g glucose/L		16 g glucose/L		32 g glucose/L	
	IBRCS	**CSTR**	**IBRCS**	**CSTR**	**IBRCS**	**CSTR**	**IBRCS**	**CSTR**
VSS reactor (mg/L)	1412	120	4552	500	9062	1245	16161	1970
VSS effluent (mg/L)	211	120	807	500	1621	1245	3370	1970
SRT (hr)	54	N/A	45	N/A	45	N/A	38	N/A
SCOD effluent (mg/L)	1659	2200	6724	8655	13400	16370	26756	34740
VFA effluent (mg/L)	1570	356	6400	1810	12820	5438	25500	7000
Total Gas (L/d)	17.1	3.4	72	19	146	61	294	76.75
Hydrogen Gas (%)	72.8	80	68	73	66.8	68	66.2	69.7
Hydrogen Gas (L/L/d)	2.5	0.5	9.8	2.7	19.5	8.3	40	10.7
pH	5.5	5.7	5.6	5.7	5.5	5.7	6	5.7

Part 2: Figure 3 shows the diurnal variation of volumetric hydrogen production rate for the biohydrogenator, with the steady-state data summarized in Table 5. After 10 days of operation on the synthetic glucose solution, when the hydrogen production rate stabilized at 9.6 ± 0.7 L H_2 / L / d, the feed was switched to corn syrup wastewater as phase 1 of operation. An organic loading rate of 26 gCOD/L/d was maintained for 30 days. As apparent from Figure 3, the change in the feed from synthetic to real waste at the same OLR did not adversely impact hydrogen production, corroborating both the success of the acclimatization phase and the lack of inhibitors in the corn syrup. The system steadily produced hydrogen at a rate of 9.8 ± 0.6 L H_2 / L / d.

The average hydrogen content in the biogas was 68 ± 4 %, with carbon dioxide as the balance. At the end of phase 1 the organic loading was doubled to 52 gCOD/L/d. The hydrogen production rate increased gradually to 20 L H_2 / L / d over a period of 6 days, with the average hydrogen production rate and hydrogen content of the biogas phase 2 of 19.3 ± 1.1 L H_2 / L / d and 60 ± 4 % , respectively. For the last 30 days of operation (phase 3), the organic loading rate was increased to 81 gCOD/L/d. After 14 days of operation the system reached a maximum hydrogen rate of 34 L H_2 / L / d. In phase 3, the average hydrogen production rate and hydrogen content of the biogas produced were 32 ± 2.3 L H_2 / L / d and 62 ± 3 %, respectively. As depicted in Figure 4, hydrogen production rate increased from 10 to 34 L H_2 / L / d with the increase of OLR from 26 to 81 gCOD/L/d.

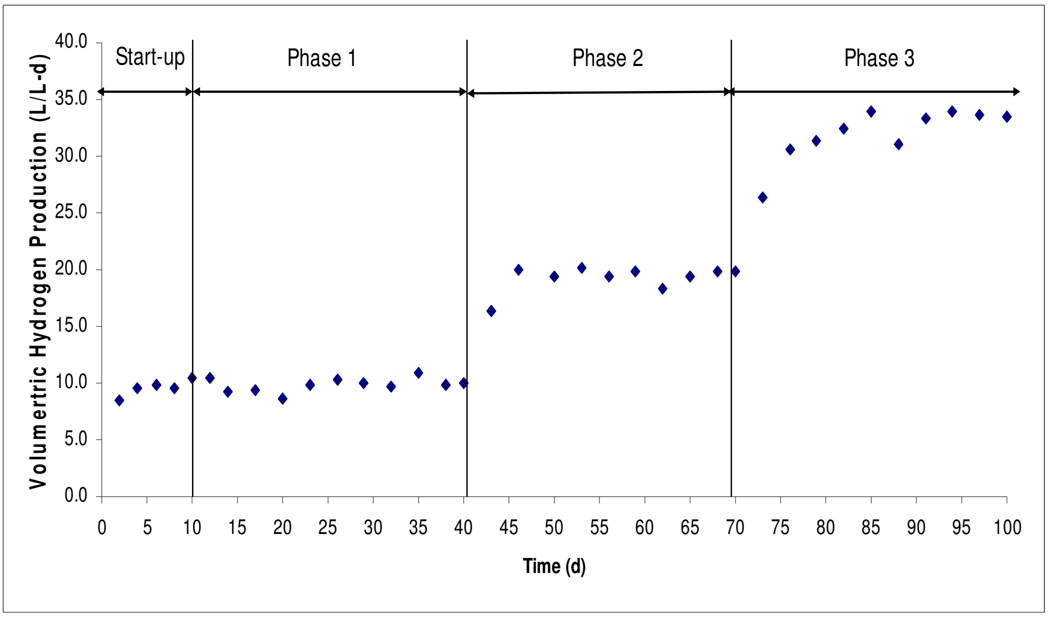


Figure 3. Temporal Variation of Volumetric Hydrogen Production rate

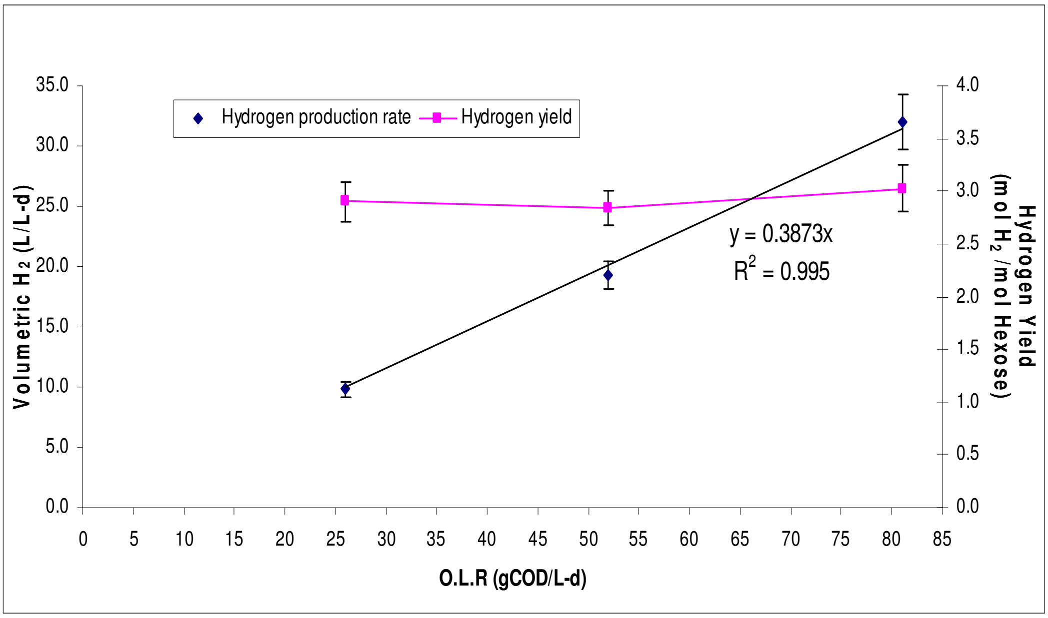


Figure 4. Relationship between Hydrogen Production Rate and Hydrogen Yield vs. OLR

The linear relationship between hydrogen production rate and organic loading rate evident from Figure 3 emphasizes the lack of substrate inhibition as well as other inhibitors in the corn syrup at OLR as high as 81 gCOD/L/d. The highest hydrogen yield achieved throughout the experimental period was 3.2 mol H_2/ mol Hexose.

Table 5. Metabolites and COD mass balance

	Phase 1	Phase 2	Phase 3
VSS (mg/L)	17226 ± 2496	23540 ± 1997	25287 ± 1879
VSS out (mg/L)	1343 ± 208	2446 ± 228	3747± 705
SCOD out (mg/L)	6125 ± 399	11753 ± 787	18189 ± 1335
Acetate (mg/L)	2647 ± 274	5139 ± 385	9060 ± 1352
Propionate (mg/L)	36 ± 16	159 ± 24	87 ± 62
Isobutyrate (mg/L)	0	0	0
Butyrate (mg/L)	1730 ± 178	2747 ± 315	3793 ± 671
Isovalerate (mg/L)	3 ± 3	50 ± 18	63 ± 25
Valerte (mg/L)	0	0	0
Ethanol (mg/L)	23 ± 9	78 ± 22	77 ± 31
Lactate (mg/L)	0	0	0
VFA (mgCOD/L)	6087 ± 579	11001 ± 529	17015± 2781
Glucose Out (mg/L)	0	0	0
Hydrogen Gas (L/d)	49 ± 3	96 ± 6	160 ± 12
Hydrogen Gas (gCOD/d) *	31 ± 2	61 ± 4	101 ± 7.5
COD balance (%) **	112 ± 6	109 ± 5	113 ± 7

* Based on 8 gCOD/g H_2
** Sample of calculation Phase 1: COD balance (%) = ((1343*1.42*15/1000+31+6125*15/1000) / (135*100)

CONCLUSIONS

Using a gravity settler after a CSTR drastically increased the hydrogen production rate and hydrogen yield from 1.8 to 9.6 L/L/d and from 1 to 2.8 mol/mol glucose, respectively. Moreover, the experiment showed that biological hydrogen production from corn-syrup using heat pre-treated anaerobically digested sludge can be achieved in the biohydrogenator. The hydrogen production rate was a function of the organic loading rate; it increased from 10 to 34 L H_2 / L / d with the increase of OLR from 26 to 81 gCOD/L/d. No inhibition of hydrogen production was observed at loadings as high as 81 gCOD/L/d. The highest hydrogen yield achieved throughout the experimental period was 3.2 mol H_2/ mol Hexose corresponds to 430 mL H_2 / gCOD and an overall average glucose to hydrogen conversion efficiency of 73 %. The decoupling of SRT from HRT in biohydrogen production systems facilitated by the superior sludge settling characteristics of hydrogen producers, evaluated in this work, validated the promise of using a gravity settler after a CSTR to maintain high biomass retention in the system and decrease biomass washout. It improved hydrogen yield and sustainability of hydrogen production, rendering it an optimum system for biological hydrogen production from waste.

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