

Increased Energetic Potential of Biohydrogen Production from Organic Municipal Wastes through Coupled Methane Generation

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ABSTRACT

The organic fraction of municipal solid waste (OFMSW) is considered a renewable source of power because of its wide availability and low-cost. Part of the energy contained in OFMSW may be 'extracted' in the form of pollution-free combustible hydrogen through anaerobic fermentation, and its energetic balance may be leaned positively by coupling a methane production stage, as demonstrated in this work. Hereby it was assessed the energy balance of coupling either a semi-continuous or batch hydrogen generation process to a methanogenic stage. In all three cases, the processes were performed on solid substrate fermentation.

Hydrogen productivity (I_{H_2}) averaged 202 NmL H_2 /kg_{wmr}/d in the semi-continuous stage (Hsc), operated at 20.9 % total solids (TS), 21 d mass retention time (MRT) and 55 °C. In the batch hydrogen stage (Hbt, operating conditions: 20.9 % TS, 50 h, 55 °C), the hydrogen yield (Y'_{H_2}) and hydrogenogenesis rate (R_{H_2}) were 1 200 mmol_{H₂}/kg_{VS} and 68.3 mmol_{H₂}/kg_{VS}/h, respectively. The methanogenic stage (M, operating conditions: 18.4 % TS, 28 d MRT, 55 °C) produced 2 023 NmLCH₄/kg_{wmr}/d. Resultant energetic potentials from the theoretical combustion of the total hydrogen and/or methane produced by all the substrate fed (in g_{dry substrate}) to the process for each stage were 256 (Hsc), 271 (Hbt) and 11 889 kJ/kg_{db} (M). Correspondingly, energetic fluxes from the combustion of the average hydrogen and/or methane production based on either H_2 or CH₄ productivity were 2.55 (Hsc), 24.11 (Hbt) and 80.25 kJ/kg_{wmr}/d (M). Indeed, coupling of M stage to Hsc and Hbt increased the energetic potential by 4 600 and 4 300 %, respectively. These results show the clear advantage of the M coupling in order to yield high energetic potential processes from wastes.

Keywords: biohydrogen; high total solids; intermittent venting; municipal organic solid wastes

1. Introduction

The world has been facing the risk of conventional oil reserves depletion and its consequent increment of prices [1].

Moreover impacts from its exploration, production, refining, handling and combustion [2, 3] affect negatively our environment. Therefore, new and environmentally friendly forms of producing energy are required. Biofuels such as biohydrogen, methane, biodiesel or even microbial fuel cells are promising alternatives [4-6]. However no single biofuel-type is expected to completely replace fossil fuel consumption. Rather, biofuels would add up to reduce fossil fuel dependence as well as environmental impacts.

Actual development in biofuels has proved their technical feasibility, which has lead to a consequent effort to evaluate both energetic and economic feasibility. Economic feasibility is influenced by the cost of the substrate, operation and plant expenses and the value of the products. One of the choices to cheapen biofuel producing processes is to use refuse or waste biomass, as there is no production cost associated to it. Agroindustrial wastes (e.g. wheat straw, corn cobs, sugarcane bagasse) and the organic fraction of municipal solid wastes (OFMSW) are well-known choices.

When producing biofuels, the type of product also influences energy feasibility, and it is expected that the energy obtained from its application to be greater than the energy input required for its production. For instance, there has been a large debate in the case of bioethanol, as there are reports that argue on the sustainability of its production as biofuel [7]. Indeed, this discussion has led to shift bioethanol production from corn to second generation cellulosic biofuels [8].

Concerning biohydrogen, its production has been assessed from different substrates such as wheat straw, wastewater, potato waste, cheese whey, cow manure, municipal solid waste, among others [9]. Yet, modest energetic gains need to be improved [10]. One strategy aimed at this purpose is to use the fermented solids from hydrogen production as substrate for a methanogenic digestion. This is biologically feasible because both hydrogen and methane are produced from complimentary stages of the anaerobic decomposition of biomass [11]. Firstly, cellulose and hemicellulose from vegetable biomass are firstly breakdown in the hydrolysis stage. Then hydrogen along with short and long chain fatty acids are produced in the acidogenic stage. In the acetogenic stage these long chain fatty acids are further fermented into acetate, which is then converted to methane in the methanogenesis stage. All these cycles occur simultaneously during simple stable anaerobic digestion with the production of sole methane. Yet by controlling acid and basic pH, hydrogen and methane coupled production has been assayed and attained from biomass [12]. However the energetic feasibility studies on OFMSW are still scarce.

Thus, the purpose of this research was evaluate from an energy standpoint the batch and semicontinuous hydrogen production coupled to a methanogenic process.

2. Materials and methods

2.1. Substrate formulation

The OFMSW was prepared of dried food wastes from local dining hall and waste office paper, in a mass concentration of 60 and 40 % w/w, respectively [12, 13]. The OFMSW had the following characteristics: pH 6.87 ± 0.21 ; total solids 93.4 ± 0.2 %; volatile solids 87.5 ± 0.5 % dry basis (db); cellulose, lignin and hemicellulose contents of 41.2 ± 7 , 09.2 ± 4.6 , 21.7 ± 3.6 % db, respectively; total Kjeldahl nitrogen 0.98 ± 0.1 % db; a ratio C/N 50.0 ± 1.5 ; Phosphorus 1848 ± 203 mg/kg_{db}; and ashes 11.9 ± 0.3 %. Previous to feeding, OFMSW was conditioned with a $\text{NaHCO}_3\text{-K}_2\text{HPO}_4$ buffer (55.7 g CaCO_3 /L) to a total solids concentration of 20.9 % w/w.

2.2. Hydrogen production (Hsc and Hbt stages)

The semi-continuous hydrogen stage (Hsc) was operated at 20.9 % total solids (TS), 21 d mass retention time (MRT) and 55 °C. Bioreactors consisted of 1 L glass bottles closed with perforated rubber stoppers for biogas outlet, and contained 500 g of biomass acclimated to OFMSW. The gas outlet was connected to a gas-sampling port and to an acid brine displacement glass bottle for measuring biogas production. Bioreactors were placed in an insulated wood-incubator with temperature control set at 55 ± 1 °C. The feeding was OFMSW at 20.9 % TS according to previous hydrogenogenic dark fermentation results.

Batch intermittently vented mini-reactors, namely SSAHF-IV were used for the batch hydrogen stage (Hbt). The mini-reactors were 250 mL glass bottles containing 48 g OFMSW (20.9% TS) and 12 g inocula acclimated to OFMSW [14, 15]. Each mini-reactor was closed with a rubber stopper through which gas sample was taken. Alike to semi-continuous reactors, batch mini-reactors were put in a wood-incubator (55 ± 1 °C).

During operation, Hsc and Hbt bioreactors were shaken twice a day for 2 min for homogenizing contents and releasing gas bubbles. The fermented solids from semi-continuous effluents in Hsc stage and those remaining after batch operation in Hbt, were preserved at 4 °C in a cold chamber for posterior feeding of the methanogenic bioreactors. All treatments were run by duplicate.

2.3. Methane production (M stage)

Methane bioreactors were fed with the fermented solids preserved from hydrogen producing stage without being subjected to any pretreatment. Operation was effected at 28 d MRT and 55 ± 1 °C in a wood-incubator. The type of semi-continuous bioreactors, agitation and biogas measurement were exactly as in Hsc stage.

2.4. Analyses

Volatile solids (VS) and total solids (TS), pH, volatile organic acids (VOA), lactic acid and solvents were analysed

as reported elsewhere [12, 16, 17]. Gas volumes were normalized (Nml or NL) to 273 K and 101.325 kPa. H₂ and CH₄ contents were determined by gas chromatography using a Molecular Sieve 5A packed column in a GOW-MAC chromatograph model 350 fitted with TCD (injector, detector and column temperatures were 37, 100 and 70°C, respectively), and argon as carrier gas.

Cellulose, lignin and hemicellulose contents in substrates were determined as reported elsewhere [16, 18] following the methods of AOAC [19]. All determinations were made by triplicate.

2.5. Energetic calculations

Two methodologies for evaluating energetic feasibility were followed: gross energetic potential (E_P) and energetic flux (E_F). The E_P accounted for the yield of energy (in Joules) from the theoretical combustion of the total hydrogen and/or methane produced by all the substrate fed (in g dry substrate) to the process during a given amount of time. Hydrogen and methane energetic potentials (E_{H_2} , E_{CH_4}) are the total hydrogen or methane production (Q_{H_2} , Q_{CH_4}) converted into energy values according to their respective ΔH_C enthalpies of combustion (Eqs. 1 and 2). The sum of both E_{H_2} and E_{CH_4} yields the gross energetic potential E_P . Then, E_P was divided by the total inflow in hydrogenogenic stage in order to obtain \hat{E}_P , which is the specific gross energetic potential per unit mass of dry substrate fed (Eq. 3). \hat{E}_P may also be expressed particularly for each stage for fairer comparisons. Combustion enthalpies considered corresponded to the higher heating values of hydrogen, 282.8 kJ/mol (141.9 kJ/g), and methane, 889.9 kJ/mol (55.6 kJ/g).

$$E_{H_2}[\text{kJ}] = \int_0^t Q_{H_2}[\text{NL/d}] dt \cdot \frac{1 \text{ mol}}{22.4 \text{ NL}} \cdot \Delta H_{C_{H_2}}[\text{kJ/mol}] \quad (1)$$

$$E_{CH_4}[\text{kJ}] = \int_0^t Q_{CH_4}[\text{NL/d}] dt \cdot \frac{1 \text{ mol}}{22.4 \text{ NL}} \cdot \Delta H_{C_{CH_4}}[\text{kJ/mol}] \quad (2)$$

$$\hat{E}_P[\text{kJ/kg}_{\text{db}}] = \frac{E_P[\text{kJ}]}{\int_0^t m_{i,H}[\text{kg/d}] \left(\frac{TS_{i,H}}{100} \right) dt} \quad (3)$$

The E_F represents a dynamic energy equivalent (in Joules per unit mass in bioreactor per day) from the combustion of the average hydrogen and/or methane production based on either H₂ or CH₄ productivity.

$$E_{F,H_2}[\text{kJ/kg}_{\text{wnt}}/\text{d}] = I_{H_2}[\text{NL/kg}_{\text{wnt}}/\text{d}] \cdot \frac{1 \text{ mol}}{22.4 \text{ NL}} \cdot \Delta H_{c,H_2}[\text{kJ/mol}] \quad (4)$$

$$E_{F,CH_4}[\text{kJ/kg}_{\text{wnt}}/\text{d}] = I_{CH_4}[\text{NL/kg}_{\text{wnt}}/\text{d}] \cdot \frac{1 \text{ mol}}{22.4 \text{ NL}} \cdot \Delta H_{c,CH_4}[\text{kJ/mol}] \quad (5)$$

Although E_P and E_F could be related, they are associated to different concepts: E_P represents the amount of energy obtained as biofuel from a unit mass of dry substrate fed to the process at the given conditions of operations. On the other hand, the E_F represents the intensity of energy obtained as biofuel. That is E_F is a dynamic representation of energy generation since it contains the variable time in its definition, so, it is not only function of the substrate fed but also is a function of the mass retention time (velocity of substrate feeding).

3. Results and discussion

Both semi-continuous and batch hydrogen production were similar in volatile solids (VS) and holocellulose content (Table 1). Reduction of VS in fermentates from Hsc and Hbt was small, considering that OFMSW had an original VS content was 87.5 % dry basis. Digestates from M stage showed a higher reduction of VS, with a consequent increase in ashes content. Such is congruent as in acidogenesis phase most biochemical reactions are fermentative, whereas in methanogenesis most of biodegradable matter has already been transformed into biogas and cells [11].

Table 1. Characterization of effluents

Parameter	Hsc ^a	Hbt ^b	M _e ^c
pH	7.43 ± 0.04	6.20 ± 0.03	10.48 ± 0.05
VS ^d (%db)	81.6 ± 0.33	78.1 ± 3.7	30.3 ± 0.20
Alkalinity ^e (mgCaCO ₃ /kg _{wb})	2309 ± 45	2583 ± 37	3595 ± 323
TKN ^f (%db)	0.84 ± 0.11	0.88 ± 0.13	1.1 ± 0.09
Cellulose (%db)	66.2 ± 0.24	64.3 ± 0.24	14.8 ± 0.81
Holocellulose (%db)	71.6 ± 0.24	69.0 ± 0.24	16.9 ± 0.24
Lignin (%db)	9.9 ± 0.24	10.8 ± 0.36	13.5 ± 0.51
Ashes (%db)	18.4 ± 0.24	20.2 ± 3.5	69.7 ± 0.24

Notes: ^a organic fraction of municipal solid waste, ^b fermented solids from the hydrogen production stage, ^c digestates from the methanogenic stage, ^d volatile solids, ^e alkalinity is expressed as mg of CaCO₃ equivalents per wet sample, ^f total Kjeldahl nitrogen.

3.1. Comparison of hydrogen production for semi-continuous and batch processes

Operation and results from the stages are shown in Table 2. Hydrogen productivity (I_{H_2}) averaged 202 NmL

$\text{H}_2/\text{kg}_{\text{wmr}}/\text{d}$ in Hsc process. In Hbt stage hydrogen yield (Y'_{H_2}) and hydrogenogenesis rate (R_{H_2}) were 1 200 $\text{mmol}_{\text{H}_2}/\text{kg}_{\text{VS}}$ and 68.3 $\text{mmol}_{\text{H}_2}/\text{kg}_{\text{VS}}/\text{h}$, respectively. Although the concepts of gas production and productivity do not apply to batch processes as they refer more likely to continuous or semi-continuous process, an adaptation of E_F calculation to batch process can be performed in order to obtain similar values only for comparison reasons. Thus, although Hbt was performed in a smaller reactor volume, when operation time was 2.5 d the hydrogen production was similar to that of Hsc and I_{H_2} was almost 10 fold higher.

Table 2. Operation and results of stages

Parameter	Hbt ^a	Hsc ^b	M ^c
t_{op} ^d (d)	2.5	21	28
Q ^e (NmL/d)	114	89.5	996
I ^f (NmL/kg _{wmr} /d)	1910	202	2 023
Y' ^g (mmol/kg _{VS})	1 200	1 485	15 800
R ^h (mmol/kg _{VS} /h)	68.3	NA	NA
E_P ⁱ (kJ/kg _{db})	271	256	11 889
E_F ^j (kJ/kg _{wmr} /d)	24.11	2.55	80.25

Notes: ^a hydrogen production batch stage, ^b hydrogen production semi-continuous stage, ^c methanogenic semi-continuous stage, ^d operation time, ^e biogas production, ^f productivity, ^g yield, ^h rate of production, ⁱ energetic potential, ^j energetic flux.

Regarding energy analysis, the energetic potentials were very similar for both processes. This indicates that hydrogenogenesis at 20.9 %TS through actual operation conditions may be reaching a maximum of hydrogen that can be extracted from OFMSW. On the other hand, Hbt had also an almost 10 fold higher E_F than Hsc due to its shorter operation time, similar to the case of I_{H_2} . When analyzing results from literature (Table 3), we found that Chu et al. [20] achieved the highest E_{P,H_2} (786 kJ/kg_{db}) and E_{F,H_2} (70.7 kJ/kg_{wmr}/d). Ours E_{P,H_2} fall in the middle of the range for similar substrates. The E_{F,H_2} from Hsc was situated in the low range, whereas Hbt showed and acceptable value next to that of semi-continuous process of Ueno et al. [21].

3.2. Methane production (M stage) and its energetic potential

M stage produced 2 023 NmLCH₄/kg_{wmr}/d from fermented solids coming out from Hsc and Hbt. Resultant E_P and E_F from the theoretical combustion of methane produced by all the substrate fed (in g dry substrate) were respectively 11889 kJ/kg_{db} and 80.25 kJ/kg_{wmr}/d (M). Indeed, the coupling of M stage to Hsc increased the E_P and E_F by 46 and 31 folds, respectively; whereas the M coupling to Hbt increased the energetic potential and flux by 43 and 3.5 fold,

Table 3. Energetic performance.

Substrate	I_{H_2}, I_{CH_4}	$E_{P,H}$ (kJ/kg)	E_{P,CH_4} (kJ/kg)	E_{F,H_2} kJ/kg _{wmr} /d	E_{F,CH_4} kJ/kg _{wmr} /d	Ref
Food wastes and paper (68.3 g/L)	2.4 L H ₂ /L/d 4.4 L CH ₄ /L/d	303	11475	30.3	175	[21]
Food wastes (100 g/L)	1.05 L H ₂ /L/d 2.4 L CH ₄ /L/d	259	16309	13.3	95	[22]
Restaurant food residues (170 g/L)	1.47 L H ₂ /L/d 2.52 L CH ₄ /L/d	701	18872	18.6	100	[23]
Simulated potato waste (10 g/L)	1.28 L H ₂ /L/d 0.67 L CH ₄ /L/d	41	1303	16.2	26	[24]
Synthetic wastewater + glucose (3 g/L)	0.19 L H ₂ /L/d 0.189 L CH ₄ /L/d	684	3094	2.5	7	[25]
OFMSW (11.7% TS)	5.6 L H ₂ /L/d 3 L CH ₄ /L/d	786	13859	70.7	119	[20]
Biowaste (2.9 %TS)	0.054 L H ₂ /L/d 2.051 L CH ₄ /L/d	29	35235	0.69	81	[26]
Cow manure and dog food (2.25 %TS)	0.125 L H ₂ /L/d 0.4 L CH ₄ /L/d	281	7847	1.58	16	[9]
OFMSW (20.9% TS) semi-continuous	0.20 L H ₂ /kg _{wmr} /d 2.02 L CH ₄ /kg _{wmr} /d	256	12145	2.55	80	This work
batch	1.798 L H ₂ /kg _{wmr} /d	271	12160	24.1	80	

respectively. These results show the clear advantage of the M coupling in order to yield high energetic potential processes from wastes. On the other hand, the inclusion of the H stage in our process is valuable since an important fraction of the E_P and E_F of the coupled H and M process could be obtained as clean fuel biohydrogen.

Still, several technologies or strategies for improving productivities and energetic yield can be pursued through: (i) selection of optimal parameters such as substrate conditioning and pretreatment, inocula selection and enrichment, (ii) influence of reactor configuration for treating high solids content organic matter, and (iii) confirmation or

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improvement of our findings at pilot scale plant tests.

4. Conclusion

- Hydrogen productivity (I_{H_2}) averaged 202 NmL H_2 /kg_{wmr}/d in the semi-continuous stage (Hsc), operated at 20.9 % total solids (TS), 21 d mass retention time (MRT) and 55 °C. In the batch hydrogen stage (Hbt, operating conditions: 20.9 % TS, 50 h, 55 °C), the hydrogen yield (Y'_{H_2}) and hydrogenogenesis rate (R_{H_2}) were 1 200 mmol_{H₂}/kg_{VS} and 68.3 mmol_{H₂}/kg_{VS}/h, respectively.
- The methanogenic stage (M, operating conditions: 18.4 % TS, 28 d MRT, 55 °C) produced 2 023 NmLCH₄/kg_{wmr}/d.
- Energetic potentials based on combustion enthalpies for the total hydrogen and methane produced by all the substrate fed (in g_{dry substrate}) to the process for each stage were 256 (Hsc), 271 (Hbt) and 11 889 kJ/kg_{db} (M).
- Indeed, coupling of M stage to Hsc increased the energetic potential 46 fold. On the other hand, the M coupling to Hbt increased the energetic potential by 43 fold. These results show the clear advantage of the M coupling in order to yield high energetic potential processes from wastes.

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Notation

E_F	energetic flux, either from hydrogen and methane stages, or total (kJ/kg _{wmr} /d)
E_P	energetic potential, either from hydrogen and methane stages, or total (kJ)
\hat{E}_P	specific gross energetic potential (kJ/kg _{db}) in Eq. 3
Hbt	hydrogenogenic batch stage
Hsc	hydrogenogenic semi-continuous stage
I	gas productivity, either from hydrogen and methane stages (NL/kg _{wrm} /d)
$m_{i,H}$	mass inflow to H-stage (g _{wb} /d)
MRT	mass retention time (d)
M	methanogenic stage
NL	volume in litres, normalized at 273 K and 101.325 kPa
NmL	volume in millilitres, normalized at 273 K and 101.325 kPa
OFMSW	organic fraction of municipal solid waste
Q_{CH_4}	methane production (NL/d)
Q_{H_2}	hydrogen production (NL/d)
TS	total solids
VOA	volatile organic acids excluding lactic acid
VS	volatile solids
Y'	gas yield, either from hydrogen and methane stages (mmol/kg _{vs})

Greek characters

ΔH_C	either hydrogen or methane combustion enthalpy (kJ/g) in Eq. 1 or 2
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Subindices

db	dry basis
ds	dry substrate
wb	wet basis
wmr	wet mass content of the reactor



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