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Short Communication

Biohydrogen and carboxylic acids production from wheat straw hydrolysate

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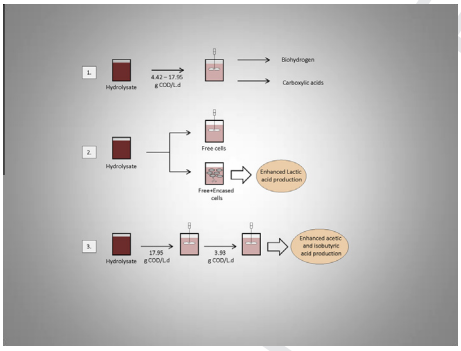
HIGHLIGHTS

- The highest biohydrogen, acetic and isobutyric acid yields were obtained at OLR of 4.42 g COD/L.d.
- 0.81 g lactic acid per g COD added was obtained at OLR of 9.33 g COD/L.d.
- The use of free and membrane-encased cells enhanced the lactic acid production by 60% at OLR of 13.42 g COD/L.d.
- A two-stage system improved the production of acetic and isobutyric acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrolyzed wheat straw was converted into carboxylic acids and biohydrogen using digesting bacteria. The fermentations were carried out using both free and membrane-encased thermophilic bacteria (55 °C) at various OLRs (4.42–17.95 g COD/L.d), in semi-continuous conditions using one or two bioreactors in a series. The highest production of biohydrogen and acetic acid was achieved at an OLR of 4.42 g COD/L.d, whilst the highest lactic acid production occurred at an OLR of 9.33 g COD/L.d. Furthermore, the bioreactor with both free and membrane-encased cells produced 60% more lactic acid compared to the conventional, free-cell bioreactor. In addition, an increase of 121% and 100% in the production of acetic and isobutyric acid, respectively, was achieved in the 2nd-stage bioreactor compared to the 1st-stage bioreactor.

1. Introduction

Lignocellulosic biomass such as agricultural and forest residues is the most abundant pool of carbohydrates on Earth (Kaparaju et al., 2009). These carbohydrates are potential feedstock for the production of biofuels and value-added chemicals (Kawaguchi et al., 2016; Pawar et al., 2013). Lignocelluloses, including wheat straw consist of hemicellulose, cellulose, and lignin and have complex and rigid structure. The building blocks of this structure, the carbohydrates, need to be cut off from the lignocellulosic complex in order to be efficiently converted into valuable products. Therefore, a pretreatment that disrupts the lignocellulosic structure is of great importance. Phosphoric acid has been used in wheat straw hydrolysis because it gathers advantages such as lower microbial toxicity for methanogenic bacteria in comparison to sulfuric acid (Chen et al., 2008) and higher sugar yields compared to peracetic acid and sodium hydroxide pretreatments (Wang et al., 2016).

Until now, there have been only a few studies on the anaerobic digestion of wheat straw hydrolysate for the concurrent produc-

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tion of biofuels and chemicals. For example, the production of biohydrogen, volatile fatty acids (VFAs), and ethanol was achieved in extreme thermophilic conditions (Kongjan and Angelidaki, 2010). In another study, biohydrogen, lactic acid, acetic acid, and ethanol were produced using anaerobic cellulolytic bacteria (Pawar et al., 2013). In such processes, the higher OLR usually corresponds to smaller reactors and lower investment costs of the bioreactors (Ren et al., 2005) as well as the energy consumption for the hydrogen production (Yu et al., 2002). Although some recent works focused on wheat straw conversion into multiple products (Kongjan and Angelidaki, 2010; Pawar et al., 2013), this is still a new and promising research area that needs further investigation.

Wheat straw hydrolysate can be digested by microorganisms that act as biocatalysts in anoxic conditions and high temperatures. This biological process is considered as being environmentally friendly and cost-effective. However, the cell wash out in the continuous process reduces the cell-density in the digester and limits the productivity. This challenge is more important for the methane production; however, the hydrogen- and acid-producing cells can also be affected if the cell wash out is intense. Membrane-enclosed cells have already been examined during anaerobic digestion (Youngsukkasem et al., 2013, 2015), but a combination of membrane-encased cells and free (suspended) cells has never been reported. This combination could give interesting results for a more flexible process in which new inoculum could be added or old cells could be replaced easily by inserting or removing the membranes.

This work aimed to investigate the concurrent production of biohydrogen and carboxylic acids from wheat straw, which had been pretreated with dilute phosphoric acid, at different OLRs. Moreover, a flexible membrane bioreactor system that contained both membrane-encased and free anaerobic cells was investigated. In addition, a second bioreactor was connected in a series with a high-OLR bioreactor in order to enhance the substrate consumption and the production of the acids.

2. Materials and methods

2.1. Liquid medium and inoculum

The commercial wheat straw (92.4% dry content) was supplied by Lantmännen Agroetanol, Norrköping, Sweden. The composition of raw wheat straw (g/g, dry basis) was: 0.048 ± 0.013 arabinan, 0.0053 ± 0.0015 galactan, 0.315 ± 0.061 glucan, 0.0047 ± 0.0011 mannan, and 0.24 ± 0.08 xylan. The wheat straw was hydrolyzed using dilute phosphoric acid (1.75%), for 10 min at 190 ± 2 °C. The hydrolysis was operated by SEKAB BioFuels & Chemicals AB (Örnsköldsvik, Sweden). Only the liquid part of the hydrolysate was used in this experiment. The composition of the liquid hydrolysate (g/L) was 32.41 sugars (18.85 ± 0.02 xylose, 5.06 ± 0.02 glucose, 4.41 ± 0.01 arabinose, 2.13 ± 0.01 cellobiose, and 1.97 ± 0.02 galactose), 8.18 ± 0.02 acetic acid, 6.16 ± 0.05 furfural, and 1.25 ± 0.02 hydroxymethyl furfural (HMF).

The composition of the inorganic macronutrients in the liquid medium was (mg/L): 280 NH_4Cl, 330 $K_2HPO_4{\cdot}3H_2O$, 100 MgSO4·7H_2O, and 10 $CaCl_2{\cdot}2H_2O$ (Osuna et al., 2003). Moreover, the concentration of the trace element stock solution was (mg/L): 2000 $FeCl_2{\cdot}4H_2O$, 50 H_3BO_3, 50 $ZnCl_2$, 500 $MnCl_2{\cdot}4H_2O$, 38 $CuCl_2{\cdot}2H_2O$, 50 $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 2000 $CoCl_2{\cdot}6H_2O$, 142 $NiCl_2{\cdot}6H_2O$, and 164 $Na_2SeO_3{\cdot}5H_2O$ (Osuna et al., 2003). Thereafter, 1 mL of this trace element stock solution was added per 1 L of the liquid medium.

The liquid medium contained wheat straw hydrolysate, micronutrients, and macronutrients (as described above) and was diluted with distilled water in order to reach a COD content of 13.25, 24.01, 27.98, 35.00, 40.25, and 53.86 g/L. The pH of the medium was adjusted to 6.0 ± 0.1 by adding sodium hydrogen carbonate.

The mixed consortium used in this study was obtained from a local thermophilic 3000-m^3 anaerobic digester operating on organic fraction of municipal solid waste (Borås Energy and Environment, Borås, Sweden). The total solids (%TS) and volatile solids (%VS) of the inoculum were 15.32% and 55.47%, respectively.

2.2. Membrane characteristics and cell-encasement

The commercial PVDF membranes were flat plain hydrophilic (Merch Millipore Ltd., Cork, Ireland), with a pore size of 0.1 μm, thickness of 125 μm, and diameter of 90 mm. Some important physicochemical characteristics of the membranes were: air flow rate of 0.15 L/min cm^2, 0.5% gravimetric extractables, 70% porosity, and water flow rate $\geqslant$0.33 mL/min cm^2. The membranes were cut into a rectangular shape (6 × 6 cm) and then folded in half and heat sealed (HPL 450 AS, Hawo GmbH, Obrigheim, Germany) on 3 sides forming an envelope of 3 × 6 cm. Then, the inoculum was placed inside the envelope through the fourth side of the membrane sachet, which was heat-sealed immediately afterwards (Youngsukkasem et al., 2012).

2.3. Reactor characteristics, seeding and start up

The reactors were serum glass bottles with plastic caps, rubber sealing, and a total volume of 600 mL (Bioprocess control AB, Lund, Sweden). They were operated as continuous stirred tank reactors (CSTR) with 100 rpm agitation rate. The temperature of the reactors was controlled at 55 ± 1 °C by a water bath.

The anaerobic culture was incubated at 55 °C for 3 days in order to consume all the nutrients and remove the dissolved methane prior to the experiment. After incubation, the excess water from the inoculum was removed by centrifugation at 10,000×*g* for 5 min (Heraeus Megafuge 8, Thermoscientific, Osterode, Germany). Thereafter, each reactor was inoculated with 45 g of anaerobic culture. In the reactor with both free and membrane-encased cells, 21 g of inoculum were loaded as free cells and 24 g were encased in polyvinylidene difluoride membrane sachets (3 g inoculum/sachet) as described in Section 2.2 (Youngsukkasem et al., 2012). After the inoculation, 300 mL of the liquid medium was added in each bioreactor. The bioreactors were then purged with pure nitrogen in order to remove any oxygen from their headspace.

2.4. Analytical methods

The total biogas production was recorded by Automatic Methane Potential Testing System (AMPTS, Bioprocess control AB, Lund, Sweden), which is based on the water displacement and has a measuring resolution of 13 mL. The produced gas volume per time unit was automatically recorded using a computer. Gas samples were collected from the reactors with a 0.25 mL gas-tight syringe (VICI, Precision Sampling Inc., Baton Rouge, LA., U.S.A.). The gas composition was analyzed every 24 h or 48 h by a Gas Chromatograph (Perkin-Elmer, Norwalk, CT., U.S.A.), equipped with a packed column (CarboxenTM 1000, SUPELCO, 6′ × 1.8″ OD, 60/80 Mesh, Shelton, CT., U.S.A.) using a thermal conductivity detector (Perkin-Elmer, Norwalk, CT., U.S.A.) with an injection temperature of 200 °C. Nitrogen was used as a carrier gas, with a flow rate of 30 mL/min at 75 °C.

The concentration of the components was measured by High-Performance Liquid Chromatography (Waters 2695, Waters Corporation, Milford, U.S.A.) with a hydrogen-based column (Aminex HPX87-H, BioRad Laboratories, München, Germany) at 60 °C and 0.6 mL/min (5 mM H_2SO_4 eluent). Moreover, the HPLC was

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equipped with a refractive index (RI) detector (Waters 2410, Waters Corporation, Milford, U.S.A.) in a series with an ultra violet (UV) absorbance detector (Waters 2487, Waters Corporation, Milford, CT., U.S.A.) at 210 nm wavelength. The calculation of the COD content was based on the liquid medium composition, which was analyzed by the HPLC.

3. Results and discussion

The dilute phosphoric acid pretreated wheat straw was anaerobically fermented at 55 °C for 29 days. During the experiment, the effect of the OLR (4.42–17.95 g COD/L.d) was studied in different CSTRs. Moreover, the efficacies of a bubble tank bioreactor that contained both free and membrane-encased cells and a CSTR with free cells were compared. In addition, a second CSTR was connected in a series to the CSTR with the highest OLR (17.95 g COD/L.d) in order to improve the efficiency of the digestion. The results from the liquid samples are presented as mean values ± standard deviation of days 11, 15, 19, 21, 25, and 27 of the fermentation.

3.1. Biohydrogen and carboxylic acids production at various OLRs

The conversion of wheat straw hydrolysate into biohydrogen and acids is investigated in the CSTRs (R1-R6) with different OLRs. The inlet characteristics and composition and the pH and carbon recovery at the outlet of the bioreactors are presented in Table 1. The HRT was 3 days, and 100 mL of the liquid digestate was replaced with fresh medium per day. The production of biohydrogen, carboxylic acids and the consumption of the wheat straw compounds are presented in Fig. 1A, E and Fig. 1B, respectively. According to Fig. 1B, the sugar consumption decreased from approx. 80% to approx. 15% as the OLR increased from 4.42 to 17.95 g COD/L.d. Moreover, for OLRs $\geqslant$8.00 g COD/L.d, the acetic acid was consumed faster than it was produced.

In Fig. 1E, the lactic acid production was close to 0.9 g/g COD added for OLR of 4.47–9.33 g COD/L.d. Furthermore, OLRs higher than 9.33 g COD/L.d seemed to inhibit the production of the lactic acid. Therefore, the limiting sugar concentration for the lactic acid production was 19.8 g/L (R4). This sugar concentration was relatively low compared to another study in which the lactic acid was produced by lactic acid bacteria at a sugar concentration of 35 g/L (Wang et al., 2015). Similar to the acetic acid production, the production of isobutyric acid was reduced, while the OLR was increased. The highest production of the isobutyric acid was recorded at an OLR of 4.47 g COD/L.d (R1). The production trends for isobutyric and acetic acid were similar because the production of isobutyric acid was accompanied by the production of acetic acid (Baroi et al., 2015).

The biohydrogen production fluctuated during the experiment, especially during the first 17 days. The highest hydrogen production was approximately 60 NmL/g COD added on the 11th day for an OLR of 4.47 g COD/L.d (R1). This biohydrogen production can also be presented as 1.3 mol H_2/mg sugars added, and it is comparable with the ratio of 5.1 mol H_2/mg glucose added that was achieved in a study of starch digestion (Arooj et al., 2008). After the 17th day, the biohydrogen production in R1 was approx. 10 NmL/g COD added until the end of the experiment.

At the OLR of 9.33 g COD/L.d, no biohydrogen production was detected after the 17th day of the digestion. Moreover, no methane production was recorded in any of the bioreactors although the acid concentration in the first two reactors was not considered inhibiting (Dogan et al., 2015). Therefore, the initial low pH value (pH 6) of the liquid medium in combination with the high OLR was possibly the main limiting factor for the methane production in this study.

Another factor that affects the microbial activity is the furan concentration (furfural and HMF). Fig. 1B shows that the higher the concentration of furfural and HMF, the lower the acetic acid and furan consumption as well as the acetic and isobutyric acid production. In addition, another study reported that a total furan concentration greater than 2 g/L inhibited the acetic acid production (Veeravalli et al., 2013). Moreover, the conversion of furfural and HMF was above 80% for OLRs of 4.42–9.33 g COD/L.d (R1-R3) and less than 70% for OLRs of 11.67-17.95 g COD/L.d (R4-R6). More specifically, the highest concentration of the furfural and HMF that was efficiently consumed was 3.54 and 0.65 g/L with 98% and 82% consumption, respectively. In another work on anaerobic digestion for methane production by enteric bacteria, there was a 50% consumption for the furfural concentrations higher than 4.43 g/L and for the HMF concentration of 2.52 g/L (Boopathy et al., 1993). Veeravalli et al. (2013) studied the effect of furfural and HMF on biohydrogen production by a mixed anaerobic culture at 37 °C, pH 5.5 and batch mode. According to the authors the highest biohydrogen yield was obtained at furfural, HMF and glucose concentrations of 0.75, 0.25 and 5 g/L, respectively. Moreover, for total furan concentration higher than 1 g/L, the biohydrogen production was decreased and there was no methane production. In this current work, the highest biohydrogen production was achieved at furfural, HMF and sugar concentrations of 0.56, 0.57 and 9.43 g/L (3.27 g/L glucose). In addition, biohydrogen was produced even for total furan concentrations of 4.19 g/L in R3 bioreactor (Table 1).

3.2. Combination of free and membrane-encased cells

In this section, a bubble tank reactor (R5.M) with both free and membrane-encased cells was examined. In addition, another CSTR (R5) with free cells was operated in parallel. The HRT of both the reactors was 3 days, and 100 mL of liquid medium was changed per day. The two bioreactors were fed with the same substrate with an OLR of 13.42 g COD/L.d. The substrate composition is presented in Table 1 (composition of R5 and R5.M). The hydrophilic

Table 1
Characteristics and composition of the inlet and carbon recovery at the outlet of the bioreactors.

Experiment	Inlet								Outlet
	OLR g COD/L.d	COD strength of medium g/L	Sugars	Acetic acid	Furfural	HMF	Lactic acid	Propionic acid	Carbon (C) recovery %
R1	4.42	13.25	9.43	1.30	0.56	0.57	–	–	90.68 ± 17.34
R2	8.00	24.01	13.95	3.45	2.80	0.50	–	–	91.19 ± 14.96
R3	9.33	27.98	15.34	4.42	3.54	0.65	–	–	94.32 ± 6.69
R4	11.67	35.00	19.18	5.52	4.43	0.83	–	–	89.03 ± 12.73
R5	13.42	40.25	24.67	5.96	3.72	0.90	–	–	82.12 ± 9.48
R6	17.95	53.86	31.25	8.02	6.04	1.23	–	–	74.16 ± 10.69
R5.M	13.42	40.25	24.67	5.96	3.72	0.90	–	–	90.71 ± 15.97
R6.1	3.93 ± 0.31	39.30	26.49 ± 1.69	5.36 ± 0.82	2.20 ± 0.45	0.46 ± 0.20	0.65 ± 0.78	0.22 ± 0.04	67.64 ± 13.09

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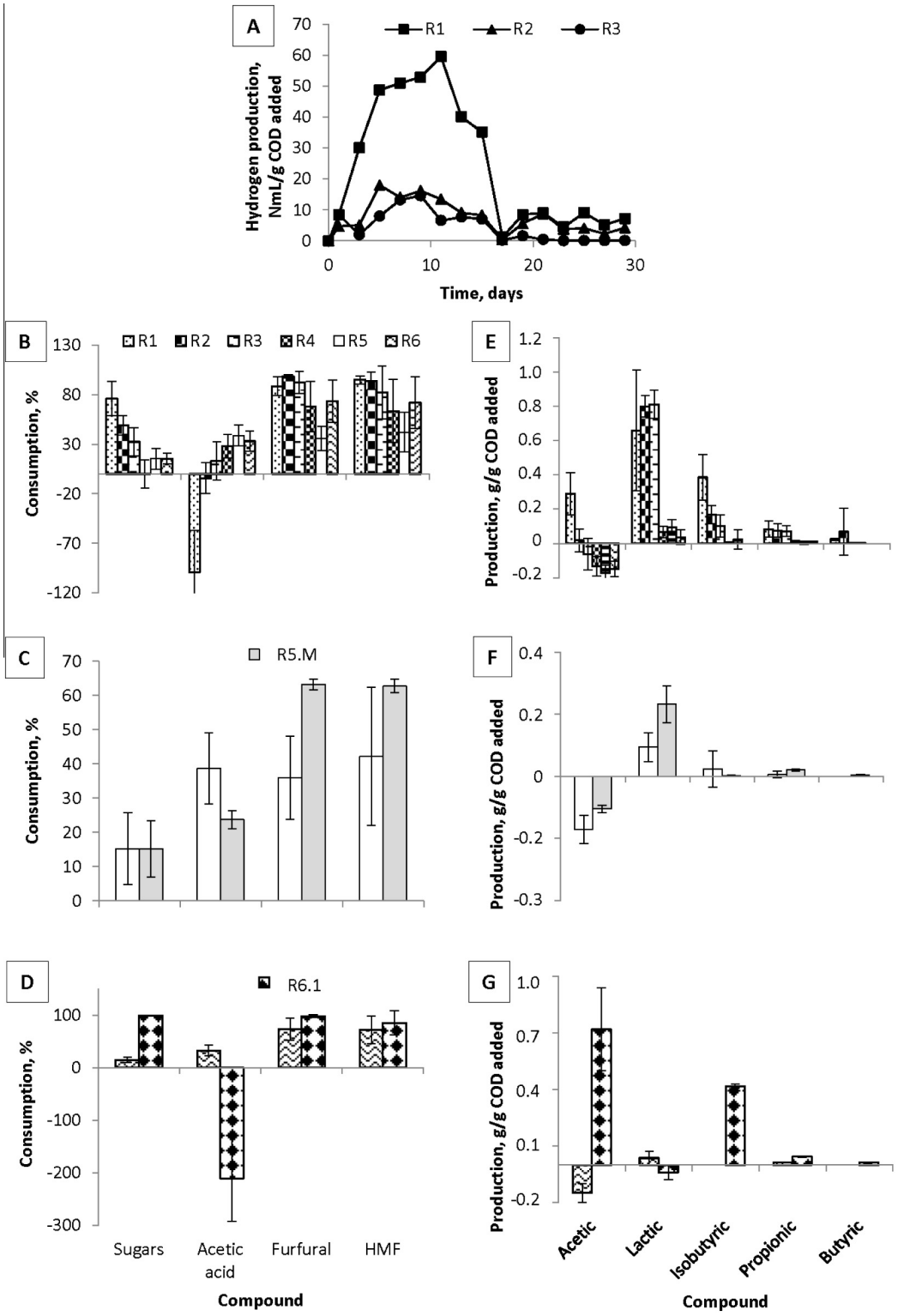

Fig. 1. Semi-continuous anaerobic digestion of wheat straw hydrolysate at 55 °C. Comparison of: (A) hydrogen production in R1-R3 (CSTRs); substrate consumption in (B) R1-R6 (CSTRs); (C) R5 (free cells) and R5.M (free+encased cells) and (D) R6 (1st-stage) and R6.1 (2nd-stage); carboxylic acids production in (E) R1–R6 (CSTRs); (F) R5 (free cells) and R5.M (free+encased cells) and (G) R6 (1st-stage) and R6.1 (2nd-stage).

PVDF membranes have been used in previous works, where they showed no inhibitory effect against the mass transfer of nutrients and biogas through their pores (Youngsukkasem et al., 2015). In this study, sugar consumption was similar in both of the reactors (Fig. 1C). This can be considered as an indication that there was no mass transfer inhibition of the sugars through the membrane pores. Moreover, a carbon mass balance between the inlet and the outlet of the bioreactors showed carbon recovery of approx. 82 and 91% at the outlet of the R5 (free cells) and R5.M (free+encased cells) bioreactor, respectively (Table 1).

Fig. 1C shows the consumption of substrate compounds and Fig. 1F the production of carboxylic acids. Interestingly enough,

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although the sugar consumption was similar in both the bioreactors, the lactic acid production was 60% higher in the membrane bioreactor. Moreover, there was a higher consumption of acetic acid in the free-cell reactor. The highest lactic acid production was probably a result of the higher consumption of furfural and HMF in the membrane bioreactor (Fig. 1C). The average lactic acid production from R5.M was 0.23 g/g COD added and it can be also presented as 0.13 g/g sugar. This value is lower but comparable with the maximum lactic acid production of 5.7 g/g sugar that was reported by Garde et al. (2002). In that study wheat straw that had been previously enzymatically hydrolyzed, was converted into lactic acid by a mix culture of anaerobic lactic acid bacteria. Studies on the anaerobic digestion of furan derivatives are scarce (Liu et al., 2015) and only one anaerobic species, *Desulphovibrio* sp., that is able to consume these furans has been isolated so far (Boopathy and Daniels, 1991). Therefore the bioconversion of furfural and HMF into valuable products such as lactic acid is an interesting result.

3.3. Enhancement of acids production in a 2nd-stage reactor

The anaerobic digestion of wheat straw in two or more stages has been mostly used in order to obtain multiple products, such as ethanol, hydrogen and methane (Kaparaju et al., 2009; Pawar et al., 2013). Another advantage of a two-stage process is that the product yields from the 1st-stage can be improved by the 2nd-stage (Colussi et al., 2013). In this work, a single stage CSTR with an OLR of 17.95 g COD/L.d (R6), showed sugar consumption of approx. 15% (Fig. 1D), while the biohydrogen and acids productions were close to zero (Fig. 1A, G). In order to enhance the acids production, 30 mL from the effluent of R6 was fed daily in a 2nd-stage bioreactor (R6.1). The OLR of the R6.1 was 3.93 g COD/L.d and the HRT, 10 days. The substrate concentrations of R6 and R6.1 are presented in Table 1.

Fig. 1D shows that 99% sugar consumption was achieved in the 2nd-stage bioreactor. Moreover, although there was no significant acids production in the 1st-stage, in the 2nd-stage reactor there was a production of 0.72 and 0.42 g/g COD added, of the acetic and isobutyric acid, respectively. This means that the acetic and isobutyric acid production was higher by 121% and 100% in the 2nd-stage bioreactor compared to the 1st-stage. The average production of acetic and isobutyric acid from this work can be alternatively presented as 0.11 and 0.06 g/g sugar, respectively. In another study of anaerobic digestion of wheat straw hydrolysate, an adapted *Clostridium tyrobutyricum* strain produced approx. 0.6 and 0.45 g/g sugar of acetic and butyric acid for a medium with pH 6 (Baroi et al., 2015). Moreover, Liu et al. (2013) reported a butyric acid yield of 0.44 g/g glucose by anaerobic digestion of wheat straw hydrolysate by the strain *C. tyrobutyricum* RPT-4213.

4. Conclusions

The results showed that the highest productions of biohydrogen, acetic and isobutyric acid were achieved for an OLR of 4.42 g COD/L.d. In addition, the maximum lactic acid production was 0.66–0.81 g/g COD added for an OLR of 4.42–9.33 g COD/L.d. A bioreactor with both free and membrane-encased cells was successfully operated for the first time and produced 60% more lactic acid than the free-cells bioreactor. Furthermore, 84% higher sugar consumption and 121% and 100% more acetic and isobutyric acid production was achieved in the 2nd-stage bioreactor compared to a 1st-stage bioreactor.

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