Biohydrogen gas production from food processing and domestic wastewaters

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Abstract

The food processing industry produces highly concentrated, carbohydrate-rich wastewaters, but their potential for biological hydrogen production has not been extensively studied. Wastewaters were obtained from four different food-processing industries that had chemical oxygen demands of 9 g/L (apple processing), 21 g/L (potato processing), and 0.6 and 20 g/L (confectioners A and B). Biogas produced from all four food processing wastewaters consistently contained 60% hydrogen, with the balance as carbon dioxide. Chemical oxygen demand (COD) removals as a result of hydrogen gas production were generally in the range of 5–11%. Overall hydrogen gas conversions were 0.7–0.9 L-H\textsubscript{2}/L-wastewater for the apple wastewater, 0.1 L/L for Confectioner-A, 0.4–2.0 L/L for Confectioner B, and 2.1–2.8 L/L for the potato wastewater. When nutrients were added to samples, there was a good correlation between hydrogen production and COD removal, with an average of 0.10±0.01 L-H\textsubscript{2}/g-COD. However, hydrogen production could not be correlated to COD removal in the absence of nutrients or in more extensive in-plant tests at the potato processing facility. Gas produced by a domestic wastewater sample (concentrated 25\times) contained only 23±8% hydrogen, resulting in an estimated maximum production of only 0.01 L/L for the original, non-diluted wastewater. Based on an observed hydrogen production yield from the effluent of the potato processing plant of 1.0 L-H\textsubscript{2}/L, and annual flows at the potato processing plant, it was estimated that if hydrogen gas was produced at this site it could be worth as much as $65,000/year.

Key words: Hydrogen production; Food processing wastewater

1. Introduction

Hydrogen gas shows great promise as a non-polluting fuel, but to reduce carbon dioxide releases hydrogen gas will need to be produced from renewable sources. Most hydrogen gas produced in the United States is obtained from thermocatalytic and gasification processes using natural gas (50%), petroleum-derived naphthenes and distillates (30%), and coal (18%), with the remainder from electricity (2%). Biological hydrogen production from the fermentation of renewable substrates is one promising alternative although the use of commercially produced food products, such as corn and sugar, is not yet economical [1]. Wastewaters show great potential for economical production of hydrogen because producing a product from a waste could reduce waste treatment and disposal costs [2].
so far been produced from the organic fraction of municipal solid wastes [3,4], damaged wheat grains [5], and cellulose [6]. Batch tests using various wastes and wastewaters suggest that hydrogen production is more efficient from carbohydrates than other materials [3,7]. Simple sugars, such as sucrose and glucose, are converted at elevated temperatures to hydrogen at high conversion efficiencies. For example, 61% of the maximum possible biological hydrogen recovery from sucrose (assuming a maximum possible yield of 8 mol-H₂/mol-sucrose) was achieved under optimum conditions of temperature (37 °C), pH, and organic loading [8]. Lower yields of 28% were obtained with glucose (maximum yield of 4 mol-H₂/mol-glucose), and 26% with sucrose, at 30 °C [7]. Hydrogen produced from molasses, lactate, and cellulose were 15%, 0.5% and 0.075%, respectively [7]. These results indicate that high-carbohydrate wastewaters will be the most useful for industrial production of hydrogen.

The $600 billion dollar food processing industry in the United States is composed of 20,000 companies [9,10], and the average large food processing industry annually produces about 1.4 billion liters of wastewater [11]. Much of the chemical oxygen demand (COD) in food processing wastewaters consists of simple sugars and starch. Food processing wastewaters have high biochemical oxygen demand (BOD) and COD values and are therefore suitable for anaerobic treatment processes [12], although many of these industries use aerobic treatment or other types of disposal systems. Two-stage systems are preferred for anaerobic wastewater treatment as they are more stable than single stage systems [13,14]. 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. Harvesting hydrogen from the first stage of a two-stage anaerobic system has not yet been explored as a method of biohydrogen production.

The purpose of this study was to investigate the potential for biohydrogen production from food processing wastewaters and domestic wastewater. Four different food processing wastewaters known to contain high concentrations of carbohydrate-rich materials were examined in batch tests to determine the hydrogen production potential based on COD content. The food processing industry wastewaters examined included those from apple and potato processing plants, and from two confectioners. Additional batch tests were conducted using potato processing wastewaters obtained from several in-plant locations. Domestic wastewater was also examined for hydrogen production as fermentation processes are increasingly being used in conjunction with nutrient control systems [15].

2. Methods

2.1. Wastewater tests

Wastewater (grab samples) was obtained at final discharge points (prior to any treatment) from an apple processor, a potato processor, and two confectioners (candy). Domestic wastewater was obtained from the outlet to the Penn State wastewater treatment plant. Preliminary tests with domestic wastewater indicated that gas production rates were low (data not shown). We suspected that glucose concentrations in the raw wastewater were insufficient to germinate the spore formers that could generate hydrogen. Therefore, the wastewater was concentrated by rotoevaporation at 100 °C to increase the concentration of organic matter in the wastewater, and the glucose and COD concentrations were measured on the final sample. All samples were kept on ice and were stored at 4 °C after collection, and warmed to room temperature (23 °C) prior to tests.

Hydrogen gas produced was measured in batch tests using a heat treated soil inoculum as previously described [7]. Soil that was being used to cultivate tomato plants was obtained from the PSU-Center of Sustainability Farms in State College, PA. This soil was baked at 100 °C for 2 h to select for heat resistant, hydrogen producing, sporeforming bacteria [8]. The heat-treated soil was sieved (354 µm opening) and one gram of the sieved mixture was added to each batch reactor (294 mL bottles; Wheaton Scientific) and buffered (0.05 M 2-(N-morpholino) ethanesulfonic acid, monohydrate) to a pH = 6.1. Bottles for the food processing wastewater tests were filled to 250 mL with either undiluted wastewater (apple processing and confectioner A), or wastewater diluted 50% with water treated by reverse osmosis (potato processing and confectioner B wastewaters). The potato processing wastewater and confectioner B wastewaters were diluted twice to reduce the COD concentration down to that of the apple processing wastewater in order to observe the hydrogen production potential of these three wastewaters at roughly the same initial COD concentration. For the domestic wastewater tests bottles were filled to 150 mL.

Preliminary analyses of nitrogen (NH₃–N) and phosphorous (PO₄) (HACH) concentrations in the wastewaters suggested that these two nutrients were limiting in all wastewaters. Therefore, the hydrogen production potential of each food processing wastewater was tested with added nutrients (N, P, and trace metals) as previously described [7] or without nutrients to determine the need for nutrient addition. All bottles were sparged with nitrogen gas for 10 min to remove dissolved oxygen. Bottles were continuously mixed using a magnetic stir bar, and gas production was measured using a respirometer system (Challenge Environmental Systems AER-200 respirometer, Fayetteville, AR). All tests were conducted at least in duplicate, and at room temperature.

Additional tests were conducted using potato processing wastewaters to obtain more detailed information on the hydrogen-production potential of specific in-plant waste streams. Wastewater samples were obtained from four different points inside the processing facility. “Gray water” samples were from water used to peel and clean the potatoes, and “Line 10” samples were collected from water used to cut and slice the potatoes. “White Water” was taken from the
Line 10 water following solids removal. “Final Sump” was the composite wastewater sent for treatment in aerated sequencing batch reactors at the plant. These additional potato wastewater tests were replicated at least five times over a 2 month period and all tests were conducted with nutrient addition. Line 10 wastewaters were much higher in COD than other in plant streams and were diluted 10 times before treatment using water treated by reverse osmosis. The wastewater was diluted so the buffering capacity (0.05 M) would maintain the pH close to 6.1.

2.2. Data analysis

Cumulative biogas production curves were obtained over the course of the batch experiment and analyzed using the modified Gompertz equation [4]:

\[ H(t) = H_{\text{max}} \exp \left\{ -\exp \left[ \frac{R \times e(t)}{H_{\text{max}}} \right] \right\} \]  

(1)

where \( H(t) \) (mL) is the amount of biogas produced at time \( t \), \( H_{\text{max}} \) (mL) the total amount of biogas produced, \( R \) (mL/h) the biogas production rate, \( e \) (h) the lag phase and \( e = 2.71828 \). Constants were obtained as previously described [8] by fitting the cumulative biogas production curves by minimizing the ratio of the sum of square error to the correlation coefficient (SSE/\( R^2 \)) using the ‘Solver’ function in Microsoft Excel version 2002.

Hydrogen gas production was calculated as previously described from headspace measurements of gas composition and the total volume of biogas produced at each time interval using

\[ V_{H,i} = V_{H,i-1} + C_{H,i}(V_{G,i} - V_{G,i-1}) \]

\[ + V_H(C_{H,i} - C_{H,i-1}) \]  

(2)

where \( V_{H,i} \) and \( V_{H,i-1} \) are cumulative hydrogen gas volumes at the current (\( i \)) and previous (\( i - 1 \)) time intervals, \( V_{G,i} \) and \( V_{G,i-1} \) the total biogas volumes in the current and previous time intervals, \( C_{H,i} \) and \( C_{H,i-1} \) the fraction of hydrogen gas in the headspace of the bottle measured using gas chromatography in the current and previous intervals, and \( V_H \) the total volume of headspace in the reactor [7].

2.3. Analytical methods

The concentration of hydrogen gas in the headspace of vessels was measured using a gas-tight syringe (0.5 mL injection volume) and a gas chromatograph (GC; Model 310, SRI Instruments, Torrence, CA) equipped with a thermal conductivity detector and a molecular sieve column (Alltech Mole sieve 5A 80/100 6’ × 1/8’ × 0.085) with nitrogen as the carrier gas. Total gas production was measured using a respirometer calibrated according to the manufacturer’s instructions. Starch (EM Science) standards were used to measure the starch concentrations in the additional potato processing wastewater tests using the phenol-sulfuric acid reducing sugar assay over a range of 20–70 mg/L [16]. CODs were measured using the HACH chemical system DR/2010. Alkalinity was measured by titration to pH 4.3, the methyl orange endpoint, using 0.5 N H\textsubscript{2}SO\textsubscript{4}.

The conversion efficiency for hydrogen production was based on the maximum possible yield of four moles of H\textsubscript{2} produced per mole of carbohydrate with the assumption that glucose was the sole carbohydrate and the primary product is acetate:

\[ C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2. \]  

(3)

COD reduction was calculated from the amount of H\textsubscript{2} produced, or directly measured according to Standard Methods [17]. The CODs of a gram of hydrogen and glucose are 8 g-COD/g-H\textsubscript{2} and 1.066 g-COD/g-glucose [15].

3. Results

3.1. Food processing wastewater tests

COD concentrations of the food processing wastewaters ranged from 0.6–21 g/L (Table 1). Based on these COD concentrations and wastewater flows, the total annual COD production at these plants was: 205, 276, 7, and 4 × 10\textsuperscript{4} kg/yr for the apple, potato, confectioner A and B wastewaters, respectively (Table 2). Confectioner A wastewater had the lowest COD concentration and yielded the least amount of biogas (0.1 L/L) of all of the food processing wastewaters (Table 2). Gas contained hydrogen at a nearly constant composition of ca. 60 ± 2% both in the presence and absence of additional nutrients for all food processing wastewaters (Table 2), with the balance of the gas composed of carbon dioxide. These hydrogen gas concentrations are similar to those obtained using sucrose and glucose-based synthetic media (62%) [7,8]. No methane gas was detected in any food processing wastewater samples.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Apple</th>
<th>Potato</th>
<th>Confectioner A</th>
<th>Confectioner B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate (m\textsuperscript{3}/h)</td>
<td>26</td>
<td>15</td>
<td>13</td>
<td>0.24</td>
</tr>
<tr>
<td>pH</td>
<td>4.3</td>
<td>6.4</td>
<td>6.3</td>
<td>4.0</td>
</tr>
<tr>
<td>COD (g/L)</td>
<td>9</td>
<td>21</td>
<td>0.6</td>
<td>20</td>
</tr>
<tr>
<td>COD (10\textsuperscript{4} kg/yr)</td>
<td>205</td>
<td>276</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1

Characteristics of the four food processing wastewaters treated in this study.
Fig. 1. Biogas production of each food processing wastewater.

Table 2
Biogas and hydrogen production for wastewater samples (±S.D.; n = number of samples)

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Nutrients</th>
<th>H$_2$ (%)</th>
<th>Biogas (L/L)$^a$</th>
<th>H$_2$ produced$^a$</th>
<th>COD removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(L-H$_2$/L)$^a$</td>
<td>L-H$_2$/g-COD</td>
</tr>
<tr>
<td>Apple (n = 4)</td>
<td>Yes</td>
<td>60 ± 2</td>
<td>1.5 ± 0.0</td>
<td>0.9 ± 0.0</td>
<td>0.100 ± 0.002</td>
</tr>
<tr>
<td>Apple (n = 2)</td>
<td>No</td>
<td>60 ± 2</td>
<td>1.1 ± 0.0</td>
<td>0.7 ± 0.0</td>
<td>0.08 ± 0.0</td>
</tr>
<tr>
<td>Confectioner-A (n = 2)</td>
<td>Yes</td>
<td>60 ± 0</td>
<td>0.1 ± 0.0</td>
<td>0.1 ± 0.0</td>
<td>0.11 ± 0.00</td>
</tr>
<tr>
<td>Confectioner-A (n = 2)</td>
<td>No</td>
<td>60 ± 0</td>
<td>0.2 ± 0.0</td>
<td>0.1 ± 0.0</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>Confectioner-B (n = 4)</td>
<td>Yes</td>
<td>60 ± 2</td>
<td>3.3 ± 0.7</td>
<td>2.0 ± 0.4</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>Confectioner-B (n = 2)</td>
<td>No</td>
<td>60 ± 2</td>
<td>0.7 ± 0.1</td>
<td>0.4 ± 0.0</td>
<td>0.020 ± 0.001</td>
</tr>
<tr>
<td>Potato (n = 3)</td>
<td>Yes</td>
<td>60 ± 2</td>
<td>3.5 ± 0.4</td>
<td>2.1 ± 0.2</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>Potato (n = 3)</td>
<td>Yes</td>
<td>60 ± 2</td>
<td>4.6 ± 0.2</td>
<td>2.8 ± 0.1</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>Domestic (n = 2)</td>
<td>Yes</td>
<td>23 ± 8</td>
<td>0.05 ± 0.01</td>
<td>0.010 ± 0.002</td>
<td>0.04 ± 0.006$^b$</td>
</tr>
</tbody>
</table>

$^a$Based on a liter of wastewater at its original strength (not diluted or concentrated).

$^b$Based on total COD concentration.
Nutrient addition did not consistently increase hydrogen gas production (Table 2). Nutrient addition significantly increased biogas production of Confectioner B \((p = 0.006)\) and apple \((p = 0.0002)\) wastewaters by 400% and 29%, respectively (Table 2). In contrast, nutrient addition decreased the potato processing wastewater biogas production by 25% \((p = 0.015)\) (Table 2). Nutrient addition appeared to decrease biogas hydrogen production by the Confectioner A, but changes were not significantly different \((p = 0.08)\).

The amount of \(H_2\) produced per liter of food processing wastewater varied widely for the different wastewaters under the test conditions, ranging from 0.1 to 2.8 L-H\(_2\)/L-WW (Table 2). Overall COD removals calculated from the loss of \(H_2\) gas \((8 \text{ g-COD/g-H}_2)\) generally was in the range of 5–11% except for one sample, where the COD removal was only 1% (Table 2). These variations in hydrogen production were in large part due to the initial COD concentration and to the presence of nutrients. In tests where nutrients were added, hydrogen production increased in proportion to COD for all wastewater except the potato wastewater (Fig. 2). The yield of hydrogen normalized by the COD concentration of the four food processing wastewaters, when nutrients were added, was constant at 0.10 ± 0.01 L-H\(_2\)/g-COD (Table 2). However, when nutrients were not added, hydrogen production varied widely \((0.10 ± 0.06 \text{ L-H}_2/\text{g-COD})\) and was not a function of the COD concentration.

The Gompertz equation was fitted to hydrogen production curves in order to estimate the biogas production rates (Fig. 3). The highest biogas production rates of 0.21 and 0.09 L-H\(_2\)/L-h were obtained with the potato and apple processing wastewaters, respectively (Table 3). The lag time prior to exponential \(H_2\) production was an average of 24 h with the exception of the potato wastewater test treated with nutrients (90 h).

3.2. Additional tests on potato processing wastewaters

Due to the high hydrogen production rates measured for the potato wastewater, additional tests were conducted using samples obtained from four different locations in the potato processing plant over several months. In these tests, both the COD and concentration of non-reducing sugars (calibrated with starch) in the wastewater were measured.

There was considerable variation in both COD and starch concentrations of the potato processing wastewaters (Table 4). Starch and COD concentrations of the potato wastewaters ranged from 1.5 and 4.8 g/L for Final Sump samples, to 32–42 g/L for Line 10 samples, respectively (Table 4). The amount of starch in the four wastewater lines varied from 30% of the COD (gray water) to 76% of the COD (Line 10).

The amount of \(H_2\) produced per liter of wastewater varied from 0.3 to 2.0 L-H\(_2\)/L-WW for the gray and white water samples, respectively (Table 4). Starch in the wastewater was nearly completely removed in all batch tests (\(> 98\%\); data not shown). The final pHS were 5.7 ± 0.3, indicating that the pH was still in the optimal range for \(H_2\) production \((5.5–6.0)\) [8].

Hydrogen production was highly variable, and was not a function of the COD concentration in these tests \((R^2 = 0.01\) for a linear regression; \(p = 0.84)\). This variability in hydrogen production is shown by an average hydrogen production, when normalized by the COD concentration, that varied by 100% \((0.07 ± 0.07 \text{ L-H}_2/\text{g-COD})\) for these different samples. Starch concentrations were also not a significant indicator of hydrogen production \((p = 0.96)\). Hydrogen yields varied from 0.02 L-H\(_2)/g-COD\) for the Line 10 wastewater to 0.21 L-H\(_2)/g-COD\) for the white water. Tests using Whitewater samples had the highest \(H_2\) production...
variability, ranging from 0.05 to 0.21 L-H$_2$/g-COD with a COD concentration of 6.7–9.8 g COD/L (Table 4).

### 3.3. Domestic wastewater

Domestic wastewater was concentrated approximately 25 times, producing a solution with a total COD of 6.2 g/L, a soluble COD of 2.6 g/L, a total glucose concentration of 342 mg/L, and a soluble glucose concentration of 294 mg/L (data not shown). The final pH of the wastewater was only slightly reduced to 5.9 ± 0.1 during fermentation tests. The concentration of hydrogen gas produced using domestic wastewater was only 23 ± 8%, a value substantially lower than that produced from the food processing wastewaters (60%) (Table 2). The total volume of biogas produced was 0.05 ± 0.01 L biogas/L wastewater resulting in only 0.010 ± 0.002 L-H$_2$/L-WW and a COD removal of 7% for the domestic wastewater (Table 2; corrected to original wastewater strengths).

### 4. Discussion

#### 4.1. Hydrogen production from wastewater

Relatively high purity hydrogen gas (ca. 60%; with the balance as CO$_2$) was produced in all batch tests with food processing wastewaters with no detectable concentration of methane gas. Samples obtained from four different food processing plants initially showed that hydrogen production was significantly related to the COD concentration of the wastewater when nutrients were added, producing 0.10 ± 0.01 L-H$_2$/g-COD. However, additional tests with wastewaters from various locations in the potato processing plant showed that in-plant variations in COD could not account for hydrogen produced using these different samples (Table 4). Starch concentrations were similarly not an accurate predictor of hydrogen production for the in-plant potato processing wastewaters.

The production of H$_2$ gas from the apple and potato processing, and confectioner A and B wastewaters accounted for a COD loss of 6 to 7% (samples containing nutrients; Table 2). These production efficiencies are lower than those of 9–17% measured for pure carbohydrates (glucose and sucrose) on the basis of COD reduction [7,8]. We suspect that the lower yields observed here for the actual wastewaters, versus pure compounds, is due to wastewater components having higher molecular weights than simple sugars as well as the particulate nature of many of the wastewater components. It is well known that polysaccharides must be cleaved into smaller molecules, typically with molecular weights less than 1000 Daltons, before they can be taken into a cell and used for energy production [18]. There are

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**Table 3**

Average kinetic constants for biogas production from food processing wastewaters

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>With nutrient addition</th>
<th>Without nutrient addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H(t)$&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$R$&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Apple</td>
<td>0.39</td>
<td>0.09</td>
</tr>
<tr>
<td>Potato</td>
<td>0.44</td>
<td>0.15</td>
</tr>
<tr>
<td>Confectioner A</td>
<td>0.03</td>
<td>0.002</td>
</tr>
<tr>
<td>Confectioner B</td>
<td>0.41</td>
<td>0.05</td>
</tr>
</tbody>
</table>

<sup>a</sup>Amount of biogas produced (L).

<sup>b</sup>Rate at which biogas was produced per liter of wastewater (L/L-h).

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**Table 4**

Characteristics, gas production, and COD removals (as H$_2$) for additional potato wastewater tests (±SD)

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Starch (g/L)</th>
<th>COD (g/L)</th>
<th>Biogas (L/L)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$H_2$ produced</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(L/L)&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Line 10</td>
<td>−1 (n = 4)</td>
<td>32</td>
<td>42</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>−2 (n = 2)</td>
<td>17</td>
<td>25</td>
<td>2.9 ± 0.0</td>
</tr>
<tr>
<td>White water</td>
<td>−1 (n = 3)</td>
<td>5.9</td>
<td>9.8</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>−2 (n = 2)</td>
<td>3.6</td>
<td>6.7</td>
<td>0.6 ± 0.0</td>
</tr>
<tr>
<td>Gray water</td>
<td>−1 (n = 2)</td>
<td>2.1</td>
<td>7.0</td>
<td>0.9 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>−2 (n = 1)</td>
<td>4.2</td>
<td>8.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>−3 (n = 3)</td>
<td>3.7</td>
<td>11</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>Final sump</td>
<td>−1 (n = 1)</td>
<td>1.5</td>
<td>4.8</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>−2 (n = 2)</td>
<td>3.4</td>
<td>10.3</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>−3 (n = 2)</td>
<td>5.7</td>
<td>14.8</td>
<td>0.8 ± 0.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Volume of gas normalized per liter of wastewater at original strength (not diluted or concentrated).
other factors that could have affected hydrogen production from the in-plant potato processing wastewaters as well. For example, disinfectants (chlorine bleach) are used during the daily cleaning period (∼ 5 pm) at the plant. Wash water sent directly to the Final Sump tank may have resulted in low hydrogen production values measured for a Final Sump sample taken at 5:30 pm. The effects of intermittent doses of disinfectants and varying carbohydrate concentration could be ameliorated through the use of an equalization tank. Clearly, additional tests will be needed to better characterize the wastewaters in order to obtain more accurate in plant predictors of hydrogen production.

Nutrient addition resulted in more consistent hydrogen production on the basis of wastewater strength (COD), but it did not always increase hydrogen production. Hydrogen production increased for two of the food processing wastewaters (apple and confectioner B wastewaters; Table 2), but was lower for the potato processing and confectioner-A wastewaters. It was expected that nutrient addition would enhance hydrogen production when using a confectioner wastewater where the main inputs are sugars and not more nutritionally well-balanced foods like apples or potatoes. This was observed for the Confectioner B wastewater as nutrient addition increased hydrogen production five fold, from 0.02 to 0.10 L-H₂/g-COD. However, no difference in hydrogen production from nutrient addition was observed with the Confectioner A wastewater, possibly due to the low amounts of hydrogen produced.

H₂ production was not a function of the COD and varied widely when using the different wastestreams within the potato processing plant. We suspect these differences are due to the macromolecular nature of the carbohydrates (i.e. simple sugars such as glucose versus high molecular weight polysaccharides). For example, the conversion of the Line 10 wastestream to H₂ had the lowest efficiency. The Line 10 wastestream had a much higher suspended solids concentration than the other wastestreams and these solids may be non-degradable at the length of time these tests were conducted. Further work is needed to understand these results.

4.2. Economic value of hydrogen

Hydrogen gas produced from food processing wastewaters could be sold, used as a heating fuel, as an off- or on-site vehicle fuel, or could be used to make electricity. Of these options, resale of the hydrogen gas makes the most economical sense. Hydrogen gas currently is sold for $6 per kg. On this basis, the annual value of the hydrogen gas for the four different industries, if produced from current wastewater concentrations and flow rates (values in Table 1) and at the amounts measured here in batch tests (Table 2), ranges from $2000 for the Confectioner B wastewater to $65,000 for the Final Sump sample of the potato processing wastewater (Table 4, 1L-H₂/L-WW, 6% COD removal). However, the hydrogen gas may have to be stripped of CO₂ and any impurities before sale and if the gas could not be used onsite, the gas would have to be compressed which would further reduce the value of the gas. The value of the H₂ gas would be lower if it were used to make electricity using a fuel cell. The value of H₂ obtained from the Final Sump wastewater sample, if converted to electricity assuming 141,586 kJ/kg for H₂ [19], 50% fuel cell efficiency, and $0.04/kWh, would be worth $9000. Thus, the hydrogen is worth only $0.80 per kg if it is used to make electricity. The value of hydrogen as a heating fuel can be calculated on the basis of its heat content and the cost of other fuels. For example, if H₂ were compared on the basis of the cost of equal heating content of methane, the hydrogen gas would annually be worth $13,000 (assuming $0.43/kg-CH₄, or $9.2 × 10⁻⁶/BTU). Since approximately 93% of the COD still remains after the H₂ fermentation, further treatment is necessary. The remaining COD could be converted to CH₄ in a second stage to recover energy remaining in the wastewater.

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