Biodegradability and methane production from secondary paper and pulp sludge: effect of fly ash and modeling

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ABSTRACT

The effect of fly ash on biodegradability and methane production from secondary paper and pulp sludge, including its modeling, was evaluated. Three tests with fly ash concentrations of 0, 10 and 20 mg/L were evaluated at 32 °C. Methane production was modeled using the modified Gompertz equation. The results show that the doses used produce a statistically significant increase of accumulated methane, giving values greater than 225 mL of CH₄ per gram of volatile solids (VS) added, and 135% greater than that obtained in the control assay. Biodegradability of VS increased 143% with respect to the control assays, giving values around 43%. The modified Gompertz model can describe well methane generation from residual sludge of the paper industry water treatment, with parameter values between those reported in the literature. Thus, the addition of fly ash to the process causes a significant increase of accumulated methane and VS removal, improving the biodegradability of paper and pulp sludge.

Key words | biodegradability, fly ash, methane production, modeling, modified Gompertz model, paper and pulp sludge

INTRODUCTION

The paper and cellulose manufacturing industry is one of Chile’s main industrial sectors, increasing its production to 4.94 million tons per year by 2008 (Rios et al. 2012). The process generates wastewater that is treated by a conventional primary–secondary treatment, which generates a secondary sludge with high moisture content composed of microbial biomass, cellulose, cell decay products, and non-biodegradable lignin precipitates (Bayr & Rintala 2012).

One way of treating this pulp and paper sludge (PPS) is anaerobic digestion (AD) to generate methane (Meyer & Edwards 2014). Several authors have explored the use of AD in order to recover or reuse secondary sewage sludge from paper mills (Karlsson et al. 2011; Lin et al. 2011; Bayr & Rintala 2012; Parameswaran & Rittmann 2012). However, the main problem regarding PPS is the low biogas production compared to other sewage sludge and the need for some form of pretreatment to enhance anaerobic digestibility (Meyer & Edwards 2014). According to the literature (Karlsson et al. 2011; Astals et al. 2013; Bayr et al. 2013; Huiliñir et al. 2014), methane yields from PPS are almost 50% lower than the values reported for methane production from municipal wastewater plants. To improve this yield, several pretreatments have been studied, including thermal, ultrasound, ozone oxidation, alkaline, enzymatic and mechanical (Elliot & Mahmod 2007); the use of zeolite as an amendment has also been reported (Huiliñir et al. 2014); however, these processes may increase the cost and cause operational problems regarding AD.

One way to avoid the pretreatment and increase the yield of AD is the use of trace elements for maximum methanogenic activity, whose importance is emphasized in the literature (Kida et al. 2001; Milan et al. 2010). A lack of sufficient nutrients and trace elements can severely limit the growth of micro-organisms and consequently the efficiency of the process (Park et al. 2010). Although the importance of this parameter is clear, its control is limited mainly by the high cost of trace salts used for this purpose. In this context, the use of a cheaper source of trace elements could help control this parameter without additional expense. A source of trace metals is fly ash, which has been applied to the AD of municipal solid waste (Lo 2005). A 3.5-fold increase in biogas production, with respect to the control, from municipal solid waste was reported (Lo et al. 2012). Even though the use of fly ash in AD of municipal solid wastes increases its...
biogas yield, the effect of the use of a solid waste rich in trace elements on the biodegradability and yield of PPS has not been studied. Therefore, the analysis of the effect of fly ash in the presence of trace elements on the AD of PPS is necessary.

Studying the kinetics of methane production from feedstock is important in the design and evaluation of anaerobic digesters. Few studies have applied mathematical models to AD using fly ash as amendment. Lo et al. (2010) reported that the modified Gompertz model can be used for modeling methane production using municipal solid waste. This was also reported by Huiliñir et al. (2014), who studied PPS AD using zeolite as amendment.

Therefore, the present work has the goal of evaluating the effect of fly ash on biodegradability and methane production from secondary PPS. The modeling of methane production using the simple modified Gompertz model was also studied.

**METHODOLOGY**

**Experimental setup**

Every experimental run considered the installation of 20 280-mL anaerobic mini-digesters with an effective operating volume of 250 mL. Thirteen of them were meant for measuring parameters in the liquid phase (chemical oxygen demand (COD), volatile solids (VS), pH); five were used to measure methane by liquid displacement using a system shown schematically in Figure 1; and two were used as controls, one without adding inoculum and one without adding secondary sludge. The mini-digesters operated in discontinuous mode for 33 days, at which time gas accumulation remained constant. Manual stirring was performed once or twice per day before reading the volume displaced by methane, besides ensuring that the balance was restored in the system.

The volume of the digesters was completed with distilled water; they were stoppered with rubber stoppers and sealed with white silicone to ensure anaerobiosis, and they were covered with aluminum foil to prevent the growth of photosynthetic organisms. All the tests were made in duplicate.

**Inoculum, substrate and experimental design**

The inoculum was obtained from an anaerobic reactor of the La Farfana water treatment plant of Aguas Andinas in Santiago, Chile. The substrate was secondary sludge from the liquid industrial residues treatment plant of Papeles Cordillera, Santiago, Chile. Table 1 shows their characteristics.

The fly ash was obtained from a thermoelectric power plant, with a particle diameter between 0.12 and 0.2 mm. Ash was taken from electrostatic precipitators used to collect particulate matter generated in the combustion of bituminous coal in thermoelectric power plants, which are placed before the gaseous effluents leave the plant. The characteristics of this ash are shown in Table 2.

The inoculum–substrate ratio was 0.15 g VS inoculum/g VS substrate in all the assays. The low inoculum–substrate ratio (high food to micro-organism ratio) had the purpose of reducing the lag-phase due to the inoculum coming from an anaerobic digester of municipal wastewater. The ash masses were 0, 2.5 and 5 mg, while the ash concentrations ([A]) were 0, 10 and 20 mg/L. For each assay, measurements were made three times per week of soluble and total COD, suspended VS, and pH. The temperature

**Table 1 | Characteristics of PPS and inoculum used in the study**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inoculum</th>
<th>PPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS (mg/L)</td>
<td>10,630.67 ± 1,307.93&lt;sup&gt;a&lt;/sup&gt;</td>
<td>–</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>16,696.67 ± 936.41&lt;sup&gt;a&lt;/sup&gt;</td>
<td>–</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>28,525 ± 2,501.67&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.12 ± 1.40 × 10&lt;sup&gt;−2&lt;/sup&gt; g&lt;sub&gt;ash&lt;/sub&gt;/g&lt;sub&gt;sludge&lt;/sub&gt;</td>
</tr>
<tr>
<td>VS (mg/L)</td>
<td>17,212 ± 654.41&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.11 ± 1.30 × 10&lt;sup&gt;−2&lt;/sup&gt; g&lt;sub&gt;ash&lt;/sub&gt;/g&lt;sub&gt;sludge&lt;/sub&gt;</td>
</tr>
<tr>
<td>pH</td>
<td>7.69</td>
<td>–</td>
</tr>
<tr>
<td>%C, dry weight</td>
<td>51.30 ± 1.50</td>
<td>51.10 ± 2.40</td>
</tr>
<tr>
<td>%N, dry weight</td>
<td>1.50 ± 1.50</td>
<td>1.50 ± 0.30</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>8.50 ± 7.50</td>
<td>34.10 ± 8.00</td>
</tr>
</tbody>
</table>

<sup>a</sup><sub>n = 6</sub>.
<sup>b</sup><sub>n = 8</sub>.
in the container was kept at 32 °C using three automatically controlled aquarium heaters.

**Chemical analyses**

The following parameters were determined: total COD, soluble COD, total and suspended solids, volatile suspended solids (VSS), and pH. COD (total and soluble) was measured by a colorimetric method according to APHA (2015), and total solids (TS), total suspended solids (TSS), VS and pH were measured according to APHA (2015).

Methane production was measured by volumetric displacement, connecting inverted falcon tubes containing 3% w/w NaOH solution to remove CO₂ and H₂S as main impurities from the biogas, displacing only the methane volume (Figure 1). The resulting biogas travels through the flexible tubing to the Falcon tube, where it comes in contact with the NaOH solution, forming sodium carbonate and bubbling only methane. The methane collected in the Falcon tube is sucked with a syringe and released in a flame to observe the presence of methane.

**Modeling of methane production**

The modified Gompertz model was used to estimate the production of methane in batch tests, which corresponds to sigmoidal functions that relate methane production with the growth of methanogenic archaea in the bio-digester (Donoso-Bravo et al. 2010; Li et al. 2012; Parameswaran & Rittmann 2012). The model is

\[
y = A \cdot \exp\left\{ - \exp\left[ \frac{\mu_m \cdot e^{(\lambda - t)}}{A} \right]\right\}
\]

where \( A \) represents potential methane production (mL CH₄/g), \( \mu_m \) is the maximum rate of methane production (mL CH₄/(g h)), \( \lambda \) is the lag time phase (h), \( y \) is the methane accumulated at time \( t \), \( t \) is the measured time (h), and \( e \) is the natural logarithm base [2.718282].

**Statistical analyses**

To determine the differences between each treatment a one-factor analysis of variance (ANOVA) was applied, using Excel 2010. The model was used to obtain calculated values of methane accumulated for every time at which experimental accumulated methane values were measured. The parameters of the model were then calculated minimizing the parameters squared (estimated error variance) using the ‘Solver’ tool from Microsoft Excel 2010. The estimated error variance was calculated as

\[
s^2 = \frac{\sum (y_i - \bar{y})^2}{N - K}
\]

where \( y_i \) is the experimental value, \( \bar{y} \) is the value calculated by the model, \( N \) is the number of samples, and \( K \) is the number of model parameters.

**RESULTS AND DISCUSSION**

**Effect of ash concentration on VS, total COD, soluble COD and pH**

Figure 2 shows the effect of ashes on VS, COD and pH. VS concentration (Figure 2(a)) decreases in all the tests, with the highest VS reduction occurring at \( [A] = 10 \) and 20 mg/L (43%). The closer values obtained between \( [A] = 10 \) and 20 mg/L show that at these concentrations the effect of ashes is always positive. The ANOVA analysis showed that there are significant differences between the assays with and without ashes (\( p < 0.05 \). Table 3 shows that at ash concentrations of 10 and 20 mg/L, VS removal was 140% higher than in the process without ashes. This higher VS
degradation can be explained by the higher microbial activity in the presence of ashes, which coincides with higher methane production (see Table 3). Even though the presence of ashes generates a greater biomass growth, the degradation of VS is greater than the production of VS by biomass growth, so the ashes improve VS degradation.

VS reduction obtained in this work is in the range found in the literature. Lin et al. (2014) got a VS reduction of 52% using PPS and monosodium glutamate, while Hagelqvist (2015) got 38–58% VS reduction using secondary PPS and municipal sewage sludge as substrates. Elliott & Mahmood (2015) obtained values between 29 and 58% of VS removal using pretreated and raw sludge. Huiliñir et al. (2014), using the same substrate and zeolite as amendment, got up to 43% of VSS removal, close to the values reported in the present paper.

Figure 2(b) shows the total COD profiles obtained in the assays. It is seen that total COD decreases in all the assays, with the highest removal at [A] = 10 mg/L (38.45%). At [A] = 10 and 20 mg/L, the COD decreases were similar up to 25 days. After that, the removal was greater at [A] = 10 mg/L. Although there are differences between [A] = 10 mg/L and 20 mg/L, in both cases COD removal was greater than the assay without ashes, increasing by 143% and 129%,

Table 3 | Yield of secondary paper sludge and percent removal of VS

<table>
<thead>
<tr>
<th>Experimental test</th>
<th>γ [mL CH₄/ gVS added]</th>
<th>Percent γ increase cf. ash = 0 mg/L</th>
<th>% VS removal</th>
<th>Percent VS increase cf. ash = 0 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash = 0</td>
<td>166.55 ± 0.34</td>
<td>-</td>
<td>30.33</td>
<td>-</td>
</tr>
<tr>
<td>Ash = 10 mg/L</td>
<td>225.55 ± 0.37</td>
<td>135.42</td>
<td>42.85</td>
<td>141.28</td>
</tr>
<tr>
<td>Ash = 20 mg/L</td>
<td>226.20 ± 0.31</td>
<td>135.82</td>
<td>42.07</td>
<td>138.84</td>
</tr>
</tbody>
</table>

Figure 2 | Variation of (a) VS, (b) total COD, (c) soluble COD and (d) pH in the process.

Figure 3 | Model’s fit with methane production in anaerobic test.
respectively. The ANOVA test showed that there are statistically significant differences between the COD obtained without ashes and with ashes ($p < 0.05$), although between $[A] = 10$ and $[A] = 20$ mg/L the same test did not show statistically significant differences, with equal profiles under this condition. Total COD removal achieved in this work, between 27 and 38%, was higher than total COD removal reported in the literature. Lin et al. (2011), working with a mixture of pulp sludge, waste-activated sludge, and monosodium glutamate, got a COD removal of around 29%. Tomei et al. (2008), using sewage sludge, got a 20% removal. Finally, Huiliñir et al. (2014), using the same substrate as in the present work, got values between 32 and 36%.

Regarding soluble COD (Figure 2(c)), it increased at first and then decreased, following the same trend as reported elsewhere (Lin et al. 2009, 2011; Huiliñir et al. 2014). This behavior can be attributed to the solubilization of particulate organic matter and the accumulation of volatile fatty acids (VFA) (Lin et al. 2011). This can also explain the experimental drop of pH at 2–7 days (Figure 2(d)). The accumulation of soluble COD at 10 days coincided with pH increase (Figure 2(d)) and methane production (Figure 3). There is a slightly different behavior in the first 8 days for the assays with $[A] = 20$ mg/L, with a decrease of soluble COD (Figure 2(c)). This behavior at 20 mg/L may be attributed to the growth of acidogenic biomass. Indeed, both total and soluble COD (Figure 2(b) and 2(c)) decrease faster at $[A] = 20$ mg/L than under the other conditions during the first 8 days, but VS do not decrease at the same rate (Figure 2(a)), showing an accumulation or increment in terms of biomass, measured as VS.

In conclusion, the use of ashes in the AD of PPS increases VS and COD removal, with the highest removal achieved at $[A] = 10$ mg/L.

### Effect of ashes on methane production

Table 3 shows the yield obtained expressed as mL CH$_4$/g of VS$_{added}$ ($\gamma$). A positive effect is seen when ashes are added, resulting also in a 135% increase with respect to the assay without ashes. The differences between the assays with ashes and without ashes were confirmed by ANOVA, where the methane yield varied significantly at the 5% level for ash additions of 10 and 20 mg/L. The increase in methane production was also reported by Lo et al. (2010); however, the increase using 20 g/L was only 6% with respect to the control. Lo et al. (2012) also showed that biogas production from municipal solid waste increases 3.5 times with respect to the control when the bioreactor was amended with ashes, a value greater than that obtained in the present work.

In general, the yields obtained in this work are similar to other results reported in the literature. Puhakka et al. (1992) determined an average production of 220 mL/g of VS$_{added}$ (570 mL/g of VS$_{removed}$) using sewage sludge from kraft pulp-mill wastewater, values slightly higher (18%) than those obtained in this work. Karlsson et al. (2011) got values between 100 and 220 mL/g of VS$_{added}$ for 20-day batch tests, with four out of six experiments with values similar to those obtained in the present work. Bayr & Rintala (2012) got values three to four times lower than those of the present work, with yields between 50 and 100 mL/g of VS$_{added}$, even operating in the thermophilic range. Lin et al. (2011), working with a co-digestion of PPS and monosodium glutamate waste liquor, got a maximum value of 200 mL/g of VS$_{added}$, 10% higher than the values obtained in the present work. The differences in these values are related to the different compositions and wastewater process used by the different plants reported by Karlsson et al. (2011). The values reported by Huiliñir et al. (2014) using the same substrate are also similar, slightly lower than those obtained with ashes.

To see if the ash effect is replicable, three new assays were carried out using $[A] = 0$, 15 and 20 mg/L (data not shown). In these assays the effect of ashes was even greater than that obtained in the previous experiments, increasing methane production up to 189%. This showed that the effect of ashes on methane production from PPS is positive at the concentrations studied.

The positive effect of trace metals on AD can be found from other authors. Gonzalez-Gil et al. (1999), using simulated wastewater with methanol as organic matter source, showed that nutrient limitations could be avoided when trace metals like Ni and Co were added continuously so that they were bioavailable for the cells at all times. Micronutrients might be present in the wastewater, but not at the required concentrations nor in bioavailable form; so the addition of a trace metal cocktail might stimulate the process. Zitomer et al. (2008), using a simulated wastewater with acetate and propionate as substrate, concluded that propionate use rates and methane production rates were more frequently stimulated by nutrient addition. Milan et al. (2010) studied the influence of different modified zeolites and metal concentrations on methane production and specific methanogenic activity (SMA) using a simulated wastewater with VFA as substrate. They concluded that heavy metal supplementation in batch digesters by modified zeolites as well as in solution increases the SMA values, and
therefore methane productivity. They also indicated that the kind of metal supplemented influences the predominance of microbial groups, where nickel and cobalt favored the presence of *Methanoseta*, while magnesium stimulated *Methanosarcina*. Pobeheim et al. (2010), using a defined model substrate for maize in anaerobic semi-continuous fermentation, showed that a limitation of nickel as well as cobalt has a negative impact on process stability and biogas production. Using levels of 0.6 and 0.05 mg/kg of fresh mass of nickel and cobalt, stable fermentation was possible up to an organic load rate of 4.3 kg COD/(m³d).

Taking into account the composition and the amount of fly ash used in the present study, the only chemical species that would have concentrations considered stimulating is manganese, as shown in Table 4.

Mn participates in the redox reactions that take place in the transformation of CO₂ into CH₄ by stabilization of methyltranferase (Oleszkiewicz & Sharma 1988), an enzyme that has been shown to be dependent on vitamin B₁₂ and is important in the biosynthesis of methane from methanol by *M. barkerii* (Patidar & Tare 2006). Conversely, Mn together with the Ca present in fly ash precipitates the excess of VFA, helping to increase the pH of the medium and avoiding or decreasing the possible toxicity of VFA in the anaerobic process (Wang et al. 2009). It is also known that the increase of the contact surface between microorganisms and substrate (provided by the fly ash in this case) contributes to improve the efficiency in any biological process, which in this case is evidenced by the increased production of methane (Fernandez et al. 2007).

### Modeling of methane production

Once the accumulated methane was obtained, the modified Gompertz model was applied as recommended in the literature (Lo et al. 2010; Huiliñir et al. 2014). The results are shown in Figure 3 and the values of the parameters obtained are given in Table 5. Although the model fits well with the data, the s² values obtained are slightly higher that those reported by Huiliñir et al. (2014).

Table 5 shows that all parameters (A, λ and μₘ) increase in all the cases in which ash was added. The greater value of A (potential methane production) is explained by the greater generation of methane in the presence of ash, while the increase of μₘ (maximum production rate of methane) may be attributed to the effect of micronutrients on methanogenic archaea.

According to the fit shown in Table 5, the highest production of methane (higher value of A) would be at an ash concentration of 20 mg/L, while the highest methane production rate (μₘ) would correspond to a concentration of 10 mg/L. The smallest increase of λ with respect to the culture without ashes would also be 10 mg/L. From the above it can be stated that the parameters of the Gompertz model agree in indicating that the best methane generation performance would occur with a dose of 10 mg/L, a situation that was found experimentally.

The modified Gompertz parameters were also determined by other studies. Donoso-Bravo et al. (2010) showed that for secondary sludge, A had a value of 245.5 mL/g of VS, similar to that obtained in the present work. With respect to μₘ, it had a value of 1.48 mL/(g VS h), 2.75 times higher than the value obtained in this work. Using paper sludge, Parameswaran & Rittmann (2002) got a value of A = 35.49 mL CH₄/g of TS, seven times lower than the value obtained in this work (272.40 mL CH₄/g of TS). Regarding μₘ, Parameswaran & Rittmann (2002) got a value of 0.64 mL/h, 2.19 times lower than the value obtained in this work (1.4 mL/h).

Huiliñir et al. (2014) using the same substrate, got μₘ = 0.415 mL CH₄/(g VS h), a value 23% lower than that obtained in the present work. Lo et al. (2010), using fly and bottom ash, got μₘ = 0.23 mL CH₄/(g VS h), a value 2.3 times lower than the results of the present work. Therefore, the values obtained are in the range presented in the literature.

### Table 4 | Metal concentration ranges (present in fly ash) considered beneficial for AD

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.002</td>
<td>0.06–64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.1</td>
<td>10–200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.01</td>
<td>0.5–20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.21</td>
<td>0.54–40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.01</td>
<td>0.005–55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 5 | Values of the parameters calculated for the different tests

<table>
<thead>
<tr>
<th>Experimental run</th>
<th>A [mL/g]</th>
<th>μₘ [mL/(g h)]</th>
<th>λ [h]</th>
<th>s²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without ash</td>
<td>177.22</td>
<td>0.38</td>
<td>52.37</td>
<td>18.13</td>
</tr>
<tr>
<td>Ash = 10 mg/L</td>
<td>239.71</td>
<td>0.54</td>
<td>72.96</td>
<td>14.79</td>
</tr>
<tr>
<td>Ash = 20 mg/L</td>
<td>246.75</td>
<td>0.47</td>
<td>87.08</td>
<td>8.49</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The addition of ash from a thermoelectric power plant in the anaerobic process at doses lower than 20 mg/L causes a significant increase of accumulated methane, VS removal, and total COD removal, improving the biodegradability of paper and pulp sludge. A concentration of 10 mg/L of fly ash gives the highest VS removal (43%) and methane production (225 mL CH₄/g VS added). The modified Gompertz model can describe well the methane generation from sewage sludge of the paper industry water treatment, with values around those reported in the literature. The kinetic constants of the modified Gompertz model at a fly ash concentration of 10 mg/L are the following: 239.71 mL CH₄/g of VS for the methane accumulated at time (A), 0.54 mL CH₄/g (h) for the maximum generation of methane (µₘₐₓ) and 87.08 h of phase lag time (λ).

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REFERENCES


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