Pre-treatment to Enhance Biogas Yield from Pulp and Paper Mill Sludge

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Abstract: The purpose of this work was to study the potential to enhance biogas production from pulp and paper mill sludge by the use of thermal pre-treatment in combination with chemical pre-treatment. Biogas from waste is a renewable fuel with very low emissions during combustion. To further reduce the use of fossil fuels, more biogas substrates are necessary. Pulp and paper mill sludge is a large untapped reservoir of potential biogas. Pulp and paper mill sludge was collected from a mill that produces both pulp and paper and has a modified waste activated sludge system as part of its wastewater treatment. Pre-treatments were chosen heat (70 °C or 140 °C) combined with either acid (pH 2 or pH 4) or base (pH 9 or pH 11, obtained with Ca(OH)₂ or NaOH). Biogas potential was tested by anaerobic digestion batch assays under mesophilic conditions. All pre-treatments were tested in six replicates. Biogas volume was measured with a gas-tight syringe and methane concentration was measured with a gas chromatograph. The methane yield from sludge subjected to thermal pre-treatment at 70 °C did not differ from the untreated sludge, but thermal pre-treatment at 140 °C had a positive effect. Within the 70 °C thermal pre-treatment group, the pH 2 acid was the most successful chemical pre-treatment, and Ca(OH)₂ pH 9 had the least effect with no measurable improvement in methane yield. For the 140 °C thermal pre-treatment group, acid and NaOH impacted methane production negatively, while the Ca(OH)₂-treated sludge did not differ from sludge with no chemical pre-treatment. In conclusion, thermal pre-treatment at 70 °C showed no effect, whereas, pre-treatment at 140 °C improved methane yield with 170%, and for this sludge additional, chemical pre-treatments are unnecessary.

Key words: Anaerobic, biogas, digestion, pre-treatment, sludge.

1. Introduction

The purpose of this work was to study the potential to enhance biogas production from pulp and paper mill secondary sludge by the use of pre-treatments. Biogas is a mixture of methane and carbon dioxide produced by anaerobic bacterial degradation of organic matter, such as sewage, manure, garbage, plants, etc.. It can be used as a fuel and is environmentally friendly as it is both renewable and produces very low emissions during combustion. Pulp and paper mill sludge is produced in the mill’s waste water treatment process. Three different types of sludges are formed: primary sludge which is mainly composed of fibers, fines and fillers, secondary sludge which contains biological microorganisms and previously unsettled fibers, and tertiary sludge which is high in chemical flocculation chemicals and also contains previously unsettled microorganisms [1, 2]. Pre-treatments aim at disrupting the integrity of the substrates, making them more susceptible to degradation, and thus increasing the biogas yield and reducing the volume of digestate.

The pulp and paper industry discards vast amounts of biomass that has been generated during wastewater treatment. The sludge produced during wastewater treatment is in some countries dumped in landfills, thus undergoing neither material nor energy recirculation. Countries with progressive environmental policies have forbidden such handling of organic materials. This biomass could be used more efficiently for energy generation and play an important role in replacing fossil fuels if it was treated properly. The two currently dominating sludge handling strategies...
Pre-treatment to Enhance Biogas Yield from Pulp and Paper Mill Sludge

are mechanical dewatering followed by composting and mechanical dewatering followed by incineration. Mechanical dewatering works well for primary sludge, but the approach is not optimal for secondary or tertiary sludges. These are difficult to dewater mechanically and thus give low energy yields when incinerated. Another approach is to minimize the amount of produced secondary sludge by prolonged aerobic digestion, which has the drawback of increasing the need for electric energy to the aerators. A third alternative is to use anaerobic digestion on the secondary sludge and by doing so extract renewable energy in the form of biogas. Furthermore, the pulp and paper industries have some processes that currently require fossil fuels, for which biogas or pure methane could become a renewable fuel alternative and thus make the mills less dependent on fossil fuels. Adding to the attractiveness of this idea is the fact that, in a previous study on energy-efficient strategies for sludge treatment it was found that anaerobic digestion is a favourable option [3].

Currently, in many countries, all available municipal sewage sludges and collected food waste are used for biogas production and more substrates are necessary in order to further reduce the use of fossil fuels. Sludge from pulp and paper mills have in previous studies [4-6] been proved useful as a feed for biogas production, especially when co-digested with nutrient-rich feeds, although it is reported to produce less methane per ton than municipal sewage sludge does [4]. Reported methane yields from pulp and paper mill secondary sludge in batch experiments under mesophilic conditions are 50 m$^3$/t VS$_{added}$ (volatile solids added) for bleached kraft pulp and paper mill secondary sludge [6], 89-197 m$^3$/t VS$_{added}$ for TMP (thermomechanical pulp) mill secondary sludge, 159 m$^3$/t VS$_{added}$ for sulphite pulp mill secondary sludge, 145 m$^3$/t VS$_{added}$ for kraft pulp mill secondary sludge and 97-199 m$^3$/t VS$_{added}$ for CTMP (chemo-thermomechanical pulp) and kraft pulp mill secondary sludge [5]. Pulp and paper mill sludge is thus a large untapped reservoir of potential biogas. Using pulp and paper mill sludge as a biogas substrate would promote the sustainable development of society, turn waste into raw material, and be in line with current bio-economic thinking.

Pre-treatment can be used to reduce the necessary retention time to produce biogas. For example, certain processes shred the substrates to increase the surface area or use a thermal pre-treatment stage to significantly enhance the biogas output. The thermal treatment can also be used to reduce the pathogenic concentration in the digestate. The aim of pre-treatment of sludge is to lyse the cell structures, which benefits especially the first step of the methane production process, the hydrolysis. Anaerobic digestion is a process driven by bacteria in an oxygen-free environment. The process is divided into three steps—hydrolysis, fermentation and methane production—in which the macromolecules are cleaved, and acid, acetate and methane are formed (Fig. 1).

In industrial anaerobic digestion, the temperature is usually between 30-40 °C or 40-60 °C, depending on whether the bacterial culture is mesophilic or thermophilic. Mesophilic digestion is more stable and demands less added heat, whereas, thermophilic digestion is faster as increased temperature increase reaction rates. Possibly mesophilic digestion in combination with pre-treatment could be a suitable compromise.

Anaerobic digestion is most often considered to be rate limited by the hydrolysis and cell lysis stages. Various sludge disintegration methods have been studied for pre-treatment purposes in order to increase the rate of methane production, including thermal, chemical, mechanical and biological methods. With pulp and paper mill secondary sludge, increased methane yields under mesophilic conditions have been reported from alkali, microwave, hydrothermal and ultrasound pre-treatments [7, 8]. Other studies show lower methane yields from pulp and paper mill sludges subjected to enzymatic, ultrasound and
microwave pre-treatments [5, 8]. Thermophilic anaerobic digestion has been shown to improve methane yields from secondary sludge compared to mesophilic anaerobic digestion [6, 9]. Under thermophilic conditions, hydrothermal pre-treatment at 150 °C has been reported to increase methane yield from 108 mL to 141 mL per g VS (volatile solids) of the untreated sludge, while the chemical pre-treatments HNO₃ pH 3 and NaOH pH 12 reduced methane yields [10]. Thermal pre-treatment at temperatures above 100 °C depolymerize larger molecules in the sludge, resulting in reduced viscosity of the slurry and increased dewaterability as the intracellular water is released from the cells [11]. At temperatures above 170 °C, persistent organic compounds inhibitory to the process forms [12]. Pre-treatment as a means to enhance methane production from pulp and paper mill sludge is further developed in Refs. [13-16].

The most studied chemical pre-treatment is the addition of sodium hydroxide (NaOH). Other bases studied include potassium hydroxide (KOH), magnesium hydroxide (Mg(OH)₂) and calcium hydroxide (Ca(OH)₂). Sodium hydroxide has been shown to have a very positive effect, often in combination with thermal pre-treatment, though high
concentrations of 10 g NaOH/L can cause the formation of persistent compounds. An alkali pre-treatment process using sodium hydroxide solution showed an optimal concentration of 8 g NaOH/100 g TS\text{sludge} (total solids of the sludge) with a methane yield of 0.32 m\textsuperscript{3}/kg VS\text{removal} (volatile solids removed by anaerobic digestion) which was 183\% of the control [17]. The disadvantages with sodium hydroxide are cost and environmental hazard. Calcium hydroxide, also known as lime, has a cost of only 6\% of the price of lye and is easier to handle, which makes it interesting as a base pre-treatment method [18]. Acid pre-treatment gives an increased solubility of the particles in the sludge, though acidic pre-treatments may, however, produce compounds that can cause inhibition and/or be toxic to methane producing anaerobic microorganisms [19].

The effect of pre-treatments on mesophilic digestion of secondary sludge from pulp and paper mills is insufficiently studied. The aim of this paper is to identify a pre-treatment in the form of thermal pre-treatment in combination with chemical pre-treatment that enhance biogas production from secondary pulp and paper mill sludge and to quantify the improved yield.

### 2. Experiments

Pulp and paper mill sludge was collected from a nearby mill that produces CTMP and kraft pulp, and wastewater treatment has a modified waste activated sludge system including an aerated lagoon. Anaerobic seed culture was collected from a mesophilic anaerobic digester at a municipal sewage treatment plant. The seed cultures were kept in 35\°C for five days, after which they had stopped producing methane.

The total solids and volatile solids of the sludges and the seed cultures are given in Table 1. Thermal pre-treatment at 140 °C affected the sludges’ TS (total solids) and VS values.

#### 2.1 Pre-treatments

Thermic pre-treatments were conducted at 70 °C or 140 °C. The temperature 70 °C is typically used for hygenisation of sludge. 140 °C was chosen to show effects of high temperature, while avoiding the formation of inhibitors. The sludge was heated in four 2.5 L metal cylinders placed in a pre-heated PEG (polyethylene glycol) oil bath, rotated there for 1 h, and then allowed to cool.

Chemical pre-treatment was conducted on the heat-treated sludge (Fig. 2). Each acid or base was added until the desired pH was reached, whereupon, the sludge was left for 1 h, then the acid or base was neutralized with NaOH or H\textsubscript{3}PO\textsubscript{4}. For acid pre-treatments, H\textsubscript{3}PO\textsubscript{4} were added to pH 2 or pH 4. Base pre-treatments consisted of NaOH or Ca(OH)\textsubscript{2} added to pH 9 or pH 11. The concentration of the chemicals used were 3 M NaOH, 3 M Ca(OH)\textsubscript{2} and 85\% H\textsubscript{3}PO\textsubscript{4}. All chemicals were analytical grade, purchased from Sigma-Aldrich.

| Table 1  Characterisation of the sludges and seed cultures regarding TS and VS. |
|----------|----------|----------|
| Sample   | TS (g/L) | VS (g/L) |
| Untreated sludge                     | 13       | 9        |
| Thermally treated at 70 °C           | 13       | 9        |
| Thermally treated at 140 °C          | 28       | 22       |
| Seed culture used for pre-treatments at 70 °C | 33       | 19       |
| Seed culture used for pre-treatments at 140 °C | 27       | 15       |

![Fig. 2 The pre-treatments examined.](image-url)
2.2 Experimental Setup

The anaerobic digestion took place in batch reactors in the form of 500 mL erlenmeyer-flasks with rubber stoppers. The stoppers were perforated with two glass tubes, one with a sampling port for the extraction of gas samples for methane content analysis, and one coupled to a gas tight bag for the collection of produced methane.

Every E-flask was put 300 mL seed culture, that had been buffered with 3.29 g NaCO$_3 \times 2$H$_2$O/L and 200 mL sludge (or water for the blanks used to test the methane production of the inoculum). Reactors with untreated sludge were used as controls. All pre-treatments and controls were tested in six replicates.

To minimize oxygen disturbance, the flasks were flushed with nitrogen gas for 30 s and then sealed with rubber stoppers connected to empty gas-tight bags. Alkalinity was adjusted by the addition to the seed culture of 3.29 g of Na$_2$CO$_3$ per liter. The initial and final pH values were measured to ensure that pH was maintained within an acceptable range. The pH values were found to be in the interval 7.0-7.3 and 6.9-7.1, respectively, which suggested that the Na$_2$CO$_3$ dosage was satisfactory.

The reactors were incubated statically in a laboratory oven at 35 °C, which corresponds to mesophilic conditions.

The duration of methane production tests has been reported to vary between 13 and 87 days with 32% of the investigated laboratories using test durations of 20 days or shorter [20]. In the current study, a test duration of 19 days was used in combination with a high inoculum to substrate ratio in order to lessen the risk of a start-up lag phase while working within an industrially feasible time frame.

2.3 Analysis

The variable of primary interest is the amount of methane produced. Produced gas volume was measured daily by emptying the gas-collecting bags with a gas-tight glass syringe of 100 mL. The methane content of the biogas was measured by using a GC (gas chromatograph) equipped with a FID (flame-ionisation detector). The GC-FID was a Clarus 480 (Perkin Elmer) fitted with a capillary column (J&W Scientific, Elite-5, 30 m × 0.25 mm × 0.25 µm) with the operating conditions: oven temperature 40 °C, injector temperature 50 °C, and detector temperature 150 °C. Helium (7.0 psi) was used as a carrier gas. The samples were collected using a Hamilton gastight 1 mL syringe. The inserted gas volume was 0.5 mL. Calibration was made with synthetic biogas for calibration purposes: geotech precision check and calibration gas 60.22 mol% methane. Methane concentration was measured every fourth day (day 2, 6, 10, 14 and 18). Upon calculation of the amount of methane gas produced, the concentration was assumed to be equal in the intervals day 1-3, 4-7, 8-11, 12-15 and 16-19.

The TS and the VS were determined for the seed culture, the untreated and thermally pre-treated sludge, and all digestates. The TS and VS values were measured in accordance with the standard APHA (American Public Health Association) methods 2,540B and 2,540E [21]. Methane yields were calculated as the amount of methane produced per VS of the untreated sludge.

3. Results and Discussion

3.1 Cumulative Biogas Production

The cumulative biogas production can be seen in Figs. 3 and 4. The inoculum: substrate ratio appears to be sufficiently high as to facilitate fast methane production in the batch reactors, as can be seen from the lack of a prolonged lag phase at the start of experiments (Figs. 3 and 4).

Thermal pre-treatment at 70 °C increased the production of biogas, with small differences for the subsequent chemical pre-treatments (Fig. 3). By itself, thermal pre-treatment at 140 °C increased biogas
Pre-treatment to Enhance Biogas Yield from Pulp and Paper Mill Sludge

Fig. 3 Cumulative biogas production from pulp and paper mill secondary sludge, thermally treated at 70 °C with or without (i.e., neutral) different pre-treatments. Untreated sludge is included for comparison.

Fig. 4 Cumulative biogas production from pulp and paper mill secondary sludge, thermally treated at 140 °C with or without (i.e., neutral) different pre-treatments. Untreated sludge is included for comparison.
production more than the 70 °C treatment did (Figs. 3 and 4). Chemical pre-treatment had a small or negative impact on the biogas production from 140 °C treated sludge (Fig. 4). The combination of 140 °C with acid or NaOH gave no more biogas than the untreated control sludge.

3.2 Methane Production

Regarding produced methane gas, the sludge subjected to thermal pre-treatment at 70 °C did not differ from the untreated sludge, but thermal pre-treatment at 140 °C had a positive effect (Fig. 5).

Within the 70 °C thermal pre-treatment group, the pH 2 acid was the most successful chemical pre-treatment, and Ca(OH)₂ pH 9 had the least effect with a methane production no different from that of sludge without any pre-treatment (Fig. 5).

For the 140 °C thermal pre-treatment group, Ca(OH)₂ pH 11 was the most successful chemical pre-treatment, but the production in those reactors did not exceed that from sludge without chemical pre-treatment. Acid impacted methane production negatively (Fig. 5).

The percentage of methane in the total biogas is higher in all the samples after heat treatment at 140 °C than in the corresponding samples at 70 °C (Table 2).

![Fig. 5 Methane production from sludge thermally treated at 70 °C or 140 °C with different pre-treatments. Reported as mL methane per VS sludge added.](image-url)
Table 2  Compilation of results with 95% confidence interval, experiments in sextuplicate.

<table>
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<th>70 °C NaOH</th>
<th>70 °C Ca(OH)₂</th>
<th>70 °C H₃PO₄</th>
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<tr>
<td>pH 11</td>
<td>558 ± 91</td>
<td>532 ± 78</td>
<td>548 ± 90</td>
<td>528 ± 92</td>
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<tr>
<td>pH 9</td>
<td>537 ± 51</td>
<td>487 ± 34</td>
<td>568 ± 74</td>
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<td>Methane/reactor (mL)</td>
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<td>303 ± 53</td>
<td>359 ± 71</td>
<td>231 ± 55</td>
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<tr>
<td>pH 9</td>
<td>314 ± 33</td>
<td>223 ± 18</td>
<td>303 ± 53</td>
<td>231 ± 55</td>
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<tr>
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<td>pH 9</td>
<td>58 ± 8.2</td>
<td>46 ± 4.9</td>
<td>53 ± 12</td>
<td>44 ± 13</td>
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Untreated 140 °C NaOH

<table>
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<tr>
<th></th>
<th>140 °C NaOH</th>
<th>140 °C Ca(OH)₂</th>
<th>140 °C H₃PO₄</th>
<th>140 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas/reactor (mL)</td>
<td>358 ± 59</td>
<td>817 ± 217</td>
<td>381 ± 74</td>
<td>782 ± 261</td>
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<tr>
<td>pH 11</td>
<td>413 ± 97</td>
<td>592 ± 203</td>
<td>421 ± 139</td>
<td>782 ± 261</td>
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<tr>
<td>Biogas/reactor (mL)</td>
<td>227 ± 45</td>
<td>613 ± 179</td>
<td>326 ± 67</td>
<td>603 ± 211</td>
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<tr>
<td>pH 11</td>
<td>257 ± 71</td>
<td>440 ± 160</td>
<td>310 ± 108</td>
<td>603 ± 211</td>
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<tr>
<td>Methane content (%)</td>
<td>63 ± 16</td>
<td>75 ± 29</td>
<td>75 ± 24</td>
<td>77 ± 37</td>
</tr>
<tr>
<td>pH 11</td>
<td>62 ± 22</td>
<td>74 ± 37</td>
<td>74 ± 35</td>
<td>77 ± 37</td>
</tr>
</tbody>
</table>

The production of 126 mL/g VS<sub>added</sub> (Fig. 5) from untreated sludge is higher than the previously reported methane yields of 53 ± 26 mL/g VS<sub>added</sub> [4] and 43 N mL/g VS<sub>added</sub> [5] in batch experiments under mesophilic conditions from this CTMP and kraft pulp mill secondary sludge, though close to the 100 mL/g VS<sub>added</sub> produced in 20 days [5] from another mill producing similar sludge. With pretreatments, the yield improved to at best 340 mL/g VS<sub>added</sub> (Fig. 5) which is an improvement by 170%.

The results regarding the effects of temperature pre-treatment agreed with what was found by Bayr [10] for thermophilic anaerobic digestion of sludge, that is, a temperature higher than 70 °C is necessary for thermal pre-treatment to be beneficial for the methane yield. The role of chemical pre-treatments is still not entirely elucidated. Previous studies show either positive effects of alkali or negative effects of both acids and alkali. In this study, acid at pH 2 seems beneficial in combination with 70 °C thermic pre-treatment, but acid had a negative effect in combination with 140 °C pre-treatment.

4. Conclusions

Pre-treatment at normal hygienization temperature did not affect the methane yield, but pre-treatment at 140 °C gave both increased production of methane per VS<sub>added</sub> and a higher methane content of the biogas. The higher methane yield achieved by this thermal pre-treatment did not require additional chemical pre-treatments.

Acknowledgments

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Pre-treatment to Enhance Biogas Yield from Pulp and Paper Mill Sludge


