Anaerobic treatability and biogas production potential of selected in-mill streams
M. I. Yang, E. A. Edwards and D. G. Allen

ABSTRACT

Biochemical methane potential assays (BMP assays) were performed to study the potential of anaerobic treatment of in-mill wastewaters. The assay results indicated that condensate and the BCTMP effluent, which are currently treated with the anaerobic internal circulation reactors, were the best streams for anaerobic treatment because of their relatively high degradability (>80%) and initial rates of biogas production. The softwood dewatering process stream was the worst with the lowest degradability (~30%). The hardwood stream was more degradable than the softwood stream from the same process. Biogas production was found to be additive and predictable in blended samples. In addition, degradability was found to be negatively correlated to the concentration of dehydroabietic acid and tannin-lignin compounds.

The anaerobic treatment of the suitable streams has great potential value with significantly reduced sludge production and energy savings.

Key words | anaerobic treatment, BCTMP effluent, methane production, pulp mill wastewater, sulphite evaporator condensate

INTRODUCTION

The pulp and paper industry is an intensively water-consuming industry (Pokhrel & Viraraghavan 2004). In Canada, effluents from a pulp and paper mill are regulated by the federal and the provincial governments, so wastewater must be treated before discharge. At present, aerobic treatment is the major secondary treatment in pulp and paper mills. However, due to the increasing production capacity of pulp and paper products, the higher costs of energy and sludge disposal, and the local legislation and environmental taxation systems, mills are seeking ways to improve their wastewater treatment systems in order to increase the treatment capacity and reduce their operating costs (Habets & Driessen 2007).

Anaerobic treatment is one option for the pulp and paper industry. Compared to aerobic treatment, anaerobic treatment has the following advantages: no aeration is required, less sludge is generated for disposal, fewer nutrients are required in the system, and the produced methane is a useful renewable fuel (Driessen & Vereijken 2005; Cakir & Stenstrom 2005). If a stream has high concentrations of organic compounds (e.g. pulp and paper streams), the energy potential associated with methane production from an anaerobic wastewater treatment can be substantial (Rittmann & McCarty 2001).

Unfortunately, not all in-mill streams are suitable for anaerobic treatment. It has been shown that the anaerobic degradability of pulp mill streams ranged from 30 to 90% (Rintala & Puhakka 1993). Some streams may contain substances that are not degradable under anaerobic conditions, or they may even cause inhibition. Therefore, the streams for anaerobic treatment should be properly selected to prevent system failure. As a result, screening for the potential of anaerobic treatment of in-mill streams is crucial.

The overall objective of this research was to evaluate the potential for anaerobic treatment of different in-mill
streams, including: 1) to study the influence of the stream type and concentration on degradation; 2) to study the importance of the stream constituent compounds on degradation; and 3) to examine the effect of blending multiple streams.

**MATERIALS AND METHODS**

**Wastewater samples**

The wastewater samples used in this study were generated from two separate pulping departments in Tembec Temiscaming, Canada, bleached chemi-thermo-mechanical pulping (BCTMP) and sulphite pulping. The BCTMP wastewater (stream B) was a combined effluent from all processes in the BCTMP department. Effluents from the dewatering process, pulp-washing process and evaporator condensate were collected from the sulphite pulping department, including: condensate (stream C), dewatering effluents (D-H for hardwood and D-S for softwood), and pulp-washing effluents (P-H for hardwood and P-S for softwood). In the mill, condensate and the BCTMP stream are currently treated using two anaerobic internal circulation (IC) reactors. The treated effluent from the IC reactors goes to the activated sludge process before discharge.

**Measurements of chemical oxygen demand (COD)**

The organic content of the stream samples was estimated by measuring the total chemical oxygen demand (TCOD) values of the samples. TCOD in each stream sample was measured following the *Standard Methods* (*APHA 1992*) in triplicates.

**Measurements of resin acids and tannin-lignin compounds**

The concentrations of resin acids and tannin-lignin compounds were measured by Testmark Laboratories Ltd. Resin acids were analyzed using HP5890/5971 GC/MS, and tannin-lignin compounds were analyzed using Bausch & Lomb Spectronic 21.

**The biochemical methane potential assay (BMP assay)**

The biochemical methane potential (BMP) assay (*Owen et al. 1979*) was selected as the main method to estimate the amount of biogas produced and the degradability of in-mill streams. In a basic BMP assay, as shown in Figure 1, the test stream sample, anaerobic inoculum and culture medium were placed in a 160-ml sealed serum bottle. The inoculum used in all assays was the same sludge collected from the IC reactors mainly treating the BCTMP stream and condensate in the mill. The detailed composition of the anaerobic culture medium was described elsewhere (*Edwards & Grbic-Galic 1994*).

An example of the assay setup is given in Table 1. The amount of stream sample utilized depended on the purpose of the assay: in the test of the effect of the stream type, the targeted concentration was ~0.8 to 1 g COD/l; in the tests of the effect of the stream concentration, the targeted concentrations were 0.6 to 3.2 g COD/l; the relative volumes of streams used for the blending assay will be described in the corresponding result section later. For each assay, a positive control and a negative control were used. As detailed in Table 1, no stream was added to the negative control. The biogas production in the negative control was due to the degradation of organics present in the inoculum solution and products from cell lysis. Therefore, the negative control served as a ‘blank’. The positive control consisted of glucose, methanol and a mixture of acetate and propionate mixed in a 1:1:1 COD ratio. Since these compounds are readily degradable, the positive control was used to monitor the state of the inoculum.

During the reaction, organic compounds were degraded to generate biogas (mainly CO₂ and CH₄), which was then  

![Figure 1](https://iwaponline.com/wst/article-pdf/62/10/2427/446186/2427.pdf)
released to the headspace. Headspace gas was sampled periodically with a lubricated glass syringe at one atmosphere pressure (1 atm). The reading of the syringe represented the amount of biogas produced between measurements. The biogas production was plotted against time. Batch experiments were terminated when there was no more new biogas production, which took roughly 4 to 5 weeks in all assays in this study. The actual biogas production was obtained by subtracting the background gas production in the negative control from the total biogas production in the assay period. The portion of the degradable organics in the waste sample was evaluated by calculating the degradability using Equations (1) and (2).

Degradability = \( \frac{\text{Actual Biogas Production}}{\text{Maximum Biogas Potential}} \times 100\% \)  

Maximum Biogas Potential = TCOD(\( g \)) × \( \frac{350 \text{ ml CH}_4}{1 \text{ g COD}} \) × \( \frac{(273 + 37) \text{ K}}{273 \text{ K}} \) × \( \frac{1 \text{ ml Biogas}}{0.7 \text{ ml CH}_4} \)  

In Equation (2), it was assumed that 70% of the biogas composition was methane. This assumption was based on the composition of the biogas produced from the IC reactors in the mill and the reported 67% CH\(_4\) content in biogas in previous studies of anaerobic wastewater treatment (Lebrato et al. 1990; Chakradhar et al. 1995; Kennedy et al. 2006).

RESULTS AND DISCUSSION

Effect of the stream type and concentration on degradability

The results of the degradability of different streams tested at multiple concentrations are illustrated in Figure 2.

The degradability varied with the stream type. The BCTMP stream and condensate, which are currently fed to the IC reactors in the mill, had the highest degradability (>80%) among all stream samples. In contrast, the softwood dewatering stream (D-S) had the lowest degradability, ranging from 20–40%. From the degradability point of view, condensate and the BCTMP effluent were the best streams for anaerobic treatment, while the softwood dewatering stream was the worst to be treated anaerobically. Although the inoculum used in the batch assays was acclimated to the BCTMP effluent and condensate in the IC reactors in the mill, additional

<table>
<thead>
<tr>
<th>Setup of BMP assays</th>
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<tr>
<td><strong>Medium</strong> (ml)</td>
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<tr>
<td>Positive control</td>
</tr>
<tr>
<td>Negative control</td>
</tr>
<tr>
<td>Test samples (triplicates)</td>
</tr>
</tbody>
</table>

Note: X is an arbitrary number, depending on the target concentration of stream in the assay.
experiments suggested that acclimation was not likely to be the major reason causing the higher degradability of the BCTMP stream and condensate; repeated refeeding (five times) of the dewatering effluents and pulp-washing effluents did not significantly enhance the degradation of these effluents (Law 2007). Therefore, the relatively low degradability of the dewatering effluents and pulp-washing effluents was more likely to be caused by the recalcitrance of some organic compounds to degradation.

Hardwood streams were more degradable than the softwood streams from the same process. The hardwood dewatering stream (D-H) and the hardwood pulp-washing stream (P-H) had degradability higher than the softwood dewatering stream (D-S) and the softwood pulp-washing stream (P-S), respectively. Therefore, it seems that hardwood streams are more suitable to anaerobic treatment than softwood streams.

The degradability of the stream was not correlated with the stream concentration, except for the softwood dewatering stream (D-S). The degradability of most of the streams remained approximately constant with respect to the stream concentration. However, in the test of the softwood dewatering stream, as the concentration increased, there was a decreasing trend in the degradability (in t-test, $p_{\text{slope}} = 0.26$ for the line), which suggests an inhibitory effect.

**Effect of the stream type on initial rate of biogas production**

The initial rates of biogas production were also estimated to investigate the effect of the stream type on anaerobic treatment of the streams. In this assay, all streams were degraded with similar initial COD concentrations. As shown in Figure 3, condensate and the BCTMP stream produced biogas significantly faster than the pulp-washing effluents (P-S and P-H) and the dewatering effluents (D-S and D-H). Therefore, from a kinetic perspective, condensate and the BCTMP effluent were the most suitable streams for anaerobic treatment. The faster degradation of condensate and the BCTMP stream was expected, as the inoculum was acclimated to these streams in the mill. In addition, it is possible that condensate and the BCTMP effluent contain more simple organic compounds that could be readily consumed by microorganisms.

**Effect of blending**

In order to make full use of the capacity of the IC reactors, there was interest studying the effect of blending other feed streams, such as the pulp-washing effluent (P-S or P-H), with condensate and the BCTMP effluent. In the mill, condensate is blended with the BCTMP stream in a 1:3 ratio before entering the IC reactors. In the BMP assays for blending, condensate (stream C) was also mixed with the BCTMP stream (stream B) in a 1:3 volumetric ratio, which was further blended with different amounts of P-S or P-H.

The biogas production was compared to the predicted production based on the degradability of the individual stream and the COD of the stream added to the sample. As illustrated in Figure 4, the actual biogas production measured from the BMP assay was similar to the prediction, suggesting that the biogas production was additive. In other words, the addition of the pulp-washing effluents (P-S or P-H) did not influence (i.e. neither inhibit nor enhance) the biogas production from condensate and the BCTMP stream in the batch assays at the tested concentrations. This suggests that we can readily predict the ultimate biogas production for blended streams. However, we noted above that the pulp-washing effluents (P-S and P-H) were degraded more slowly and were less degradable than condensate and the BCTMP effluent, especially the
softwood pulp-washing effluent. Consequently, blending the pulp-washing effluent to condensate and the BCTMP stream to increase overall methane recovery may cause a build up of undegradable, and possibly inhibitory compounds in the IC reactors, which may be deleterious to the microorganisms and eventually cause operational failure. Therefore, in order to confirm the preliminary conclusions of blending drawn from this batch study, further research should be carried out to study the long term effects of exposure to compounds present in the pulp-washing stream on the microbial community. In addition, since aggregation of biomass is important for retention of microorganisms in high rate anaerobic reactors, the effect of blending on microbial aggregation should also be investigated.

Linking chemical analysis with biogas production

In order to understand the reasons for the difference in degradability of the various stream samples, the constituent compounds and their concentrations were analyzed. Adsorbable organic halogen (AOX), sulphate, sulphite, ammonium, long-chain fatty acids, resin acids, and tannin and lignin compounds have been proposed to be problematic to anaerobic degradation in literature (Puhakka et al. 1985; Sierra-Alvarez & Lettinga 1991; Sierra-Alvarez et al. 1991). The concentrations of these compounds in the BCTMP stream, condensate, dewater effluents and pulp-washing effluents were measured (Yang 2008). The concentrations of these compounds in all samples fed with a single stream (i.e. all samples presented in Figure 2) were calculated. The calculated concentrations were plotted against the degradability of the sample for each compound. No correlation was found for any compounds except in the cases of dehydroabietic acid (DHA) (Figure 5) and tannin-lignin compounds (Figure 6).

Degradability was negatively correlated with the concentrations of DHA and tannin-lignin compounds. As shown in Figure 5, as the DHA concentration increased, the degradability of the stream samples decreased. As shown in Figure 6, a sample containing more...
Tannin-lignin compounds had a lower degradability. Softwood effluent contained more DHA and tannin-lignin compounds than the hardwood effluent from the same process. The greater amounts of DHA and tannin-lignin compounds in the softwood effluents could be one reason for the lower degradability of the samples containing these streams.

A positive linear correlation was also found between DHA concentration and tannin-lignin concentration, so it was difficult to separate the effect of DHA from that of tannin-lignin compounds on degradation. A low degradability can be caused by inhibition of the compounds to anaerobic degradation, or the recalcitrance of the compound to degradation. Since DHA contributed to no more than 2% of the total added COD in all test samples, the low degradability of a sample (e.g. D-S) was unlikely to be due to the resistance of DHA to degradation. Previous studies have shown that a DHA concentration of 49 mg/l could inhibit the activity of methanogens by 50% (IC\textsubscript{50}) (Sierra-Alvarez & Lettinga 1991). In the sample where the most softwood dewatering effluent was added and the lowest degradability was observed, the DHA concentration reached as high as 29.2 mg/l, which was higher than half of the IC\textsubscript{50}. Therefore, the inhibitory effect of DHA could be one reason for the low degradability. On the other hand, the IC\textsubscript{50} values of tannins and lignins were compound-specific, ranging from 330 to 5,650 mg/l. Previous studies have shown that low molecular weight lignin compounds could be inhibitory, while high molecular weight lignin compounds were non-inhibitory but undegradable (Sierra-Alvarez et al. 1991). A detailed constituent composition would be required to determine the role of tannin and lignin compounds in our degradability study. However, since the concentration of tannin and lignin compounds was measured as a group (mg/l), detailed analysis of the data was not possible. Nineteen lignin model compounds (Sierra-Alvarez et al. 1991) and three tannin compounds (Hagerman et al. 1998) were used to estimate the percentage of lignin-tannin compounds in

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### Table 2: Anaerobic-aerobic treatment vs conventional aerobic treatment

<table>
<thead>
<tr>
<th>Wood type of pulp-washing effluent</th>
<th>Total CH\textsubscript{4} production (m\textsuperscript{3}/d)</th>
<th>Total sludge production (ton/d)</th>
<th>Sludge reduction based on completely aerobic treatment (%)</th>
<th>Increase in CH\textsubscript{4} based on current operation (%)</th>
<th>Sludge reduction based on current operation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No anaerobic at all (aerobic only)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S.W.</td>
<td>0</td>
<td>21.5</td>
<td>Used as the reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H.W.</td>
<td>0</td>
<td>21.7</td>
<td>Used as the reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anaerobic for streams C and B (current)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S.W.</td>
<td>36,000</td>
<td>8.7</td>
<td>60</td>
<td>Used as the reference</td>
<td>Used as the reference</td>
</tr>
<tr>
<td>H.W.</td>
<td>36,000</td>
<td>8.9</td>
<td>59</td>
<td>Used as the reference</td>
<td>Used as the reference</td>
</tr>
<tr>
<td>Anaerobic for streams C and B, as well as P-S or P-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S.W.</td>
<td>44,000</td>
<td>5.7</td>
<td>73</td>
<td>22</td>
<td>34</td>
</tr>
<tr>
<td>H.W.</td>
<td>48,000</td>
<td>4.5</td>
<td>79</td>
<td>33</td>
<td>50</td>
</tr>
</tbody>
</table>

**Note:** Since the cell yield in anaerobic treatment is very small, the biomass synthesis from anaerobic treatment was neglected in the calculation. The total sludge production represents the sludge produced in the activated sludge process. The aerobic cell yield was assumed to be 0.42 g VSS/gBOD. BOD was estimated as (1/3) of the COD. A complete degradation of BOD was also assumed for the aerobic treatment.
the added COD. It was found that the tannin-lignin compounds present in the sample contributed to 13 to 26% of the total COD addition. Because of the substantial percentage of COD, the low degradability in the presence of tannins-lignins was more likely due to the resistance of the compounds to degradation. Nevertheless, more detailed analysis of tannin and lignin compounds, as well as the changes in the compound concentration during the assays, is required to confirm the role of the tannin and lignin compounds in anaerobic treatment of the in-mill streams.

**Sludge production and CH₄ production: anaerobic-aerobic treatment vs. conventional aerobic treatment**

Based on the degradability results in this research, a preliminary estimation of the methane production and the sludge production from a two-stage anaerobic-aerobic treatment were calculated, demonstrating the outstanding potential for further application of this technology to a wider range of in-mill streams. The sludge production from a conventional aerobic treatment was also estimated for comparison. As shown in Table 2, when treating condensate and the BCTMP effluent anaerobically, a significant amount of methane can be generated, and the sludge production can be reduced by more than half compared to the case of sole aerobic treatment. If the pulp-washing stream (Stream P-S or P-H) is blended in, a further significant increase in methane production and sludge reduction, compared to the current treatment, can be achieved.

**CONCLUSIONS**

The BMP assay results demonstrated that condensate and the BCTMP effluent were the most suitable streams for anaerobic treatment because they have the highest degradability (>80% of the COD) and the fastest initial biogas production rate. In contrast, the softwood dewatering process stream was the least degradable and its degradability dropped as the stream concentration increased, suggesting an inhibitory effect. More experiments need to be performed to support this conclusion of the potential inhibition of the softwood dewatering stream. The degradability test also showed that the hardwood stream was more degradable than the softwood stream from the same process. Furthermore, blending multiple streams (i.e. condensate and the BCTMP stream with the pulp-washing effluent) did not change the degradability of the constituent streams, so the biogas production was additive, implying that the effect of mixing streams into the IC reactors can be predicted based on the results of individual stream. Nevertheless, the addition of new streams should be tested at the pilot scale to study the application of these batch results to full scale implementation. In particular, the long term effects of the microorganisms being exposed to the new streams should be evaluated. Dehydroabietic acid concentration and tannin-lignin concentration were both negatively correlated with degradability. Further research is recommended to perform more detailed analysis of the stream constituents, such as analyzing the concentrations before and after the treatment, to confirm the role of dehydroabietic acid and tannin-lignin compounds in anaerobic treatment. In addition, pretreatment studies to enhance the degradability of these streams are recommended.

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