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Evaluation of a pretreatment process for improved methane production from grass silage

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Abstract

Hydrolysis is a rate limiting step in anaerobic digestion. Hydrolytic pre-treatment of grass silage was evaluated at thermophilic temperature (55 °C), and the effect of organic loading rates (OLR) and hydraulic retention time (HRT) was studied. Two lab scale stainless steel continuously stirred reactors (10 L) and 12 glass reactors (2 L) were used. The OLR of 6.5, 5, 2.5 Kg VS m\textsuperscript{-3} d\textsuperscript{-1} at HRT of 10, 6, 4, 2 days were evaluated respectively. The parameters assessed as hydrolysis indicators were volatile solids (VS) destruction, volatile fatty acids (VFA) and soluble chemical oxygen demand (sCOD). Biological methane potential (BMP) tests were carried out at mesophilic temperature (38°C) for the evaluation of the effect of hydrolysis on the methanogenic phase of anaerobic digestion. A range of methane production from 0.22 to 0.400 m\textsuperscript{3} CH\textsubscript{4} (STP) gVS\textsuperscript{-1} was obtained from BMP assays.

1. Introduction

In anaerobic digestion (AD) of biomass, hydrolysis is considered a rate limiting step [1,2]. This makes the biogas production highly dependent on the hydrolysis rate of AD [3]. Two-stage anaerobic digestion systems have several advantages over conventional processes such as

- They permit the selection and enrichment of different microorganisms in each digester [4].
- They increase the stability of the process by controlling the acidification stage in order to prevent overloading and build-up of toxic materials [3].
- The first stage may act as a metabolic buffer, preventing pH shock to the methanogenic population [5].

The optimum environmental and operational parameters influencing the acid-phase digestion should be determined for each particular waste. Among the operational parameters, hydraulic retention time (HRT) is an important variable in two-stage anaerobic digestion process [5-7]. The pH is also an important variable for providing a stable and more favourable substrate for the methanogenic step. Several authors suggest that the optimal pH for a better hydrolytic and acidogenic bacteria activity ranges between 5 and 6 [1,8-10].

Despite the widespread deployment of agricultural digesters digestion energy crops including grass silage; optimal digestion of grass silage is an area still under active research [3]. Most of the work on optimising grass silage digestion is conducted at laboratory and pilot scale [4]. The interest in using grass silage as a feedstock for bioenergy and biorefinery systems is due to its high yield potential in terms of methane production per hectare [2,4].

As part of an examination of feasible pretreatment methods, we have tested thermophilic anaerobic hydrolysis. The aim of this study is to optimise a thermophilic anaerobic hydrolysis step for grass silage as a part of a two-stage anaerobic digestion system. The effect of the
operational conditions such as HRT and OLR on the VFA, sCOD, VSD and BMP were evaluated using completely mixed reactors.

2. Materials and Methods

2.1. Sample preparation

Small square bails of silage (25 Kg), of first cut perennial ryegrass as digester substrate were provided by Irish Agricultural Institute 'Teagasc', Grange Research Centre, Dunsany, Co Meath Ireland. The silage was dried at 60 °C in a rotating drum with heated air. The dried silage was milled using an electrical meat mincer to pass through a 3.5 mm sieve. The solids composition of the silage after drying was 907.34 g TS Kg⁻¹ and the volatile solids (VS) content was 828.39 g VS Kg⁻¹.

2.2. Hydrolysis Reactors

Stainless Steel Reactors: Experiments were carried out in two continuously stainless steel reactors (CSTR) with a working volume of 9 L. The reactors were operated at an OLR of 2.5 Kg VS m⁻³ d⁻¹ for HRT of 6, 4 and 2 days. The reactors were mixed mechanically with an electric overhead stirrer with controllable speed and stainless steel paddles. The temperature was maintained at 55°C using a hot plate (Heidolph MR3001K) with integrated temperature control (Heidolph EKT 3001).

Glass reactors: 12 glass reactors with a working volume of 1.5 L were used. The reactors were continuously agitated using magnetic stirrers (Stuart stir SB161). The temperature of the reactors was controlled by immersion in a water bath kept at a constant temperature (55 °C). The biogas produced was collected in glass columns by downward displacement of water acidified at pH 2.0 with HCL and 10% NaCl.

Both types of reactors were fed once a day and purged with nitrogen for 2 minutes in order to maintain anaerobic conditions. Each condition was run for at least 3 HRT, after 5 days of adaptation.

2.3. Seed Inoculum

Inoculum was obtained from a single stage mesophilic anaerobic digester of cattle slurry at AFBI, Northern Ireland. The digestate had VS content of 24.8 g VS Kg⁻¹ after passing trough a 2 mm sieve. This sludge was used for BMP tests and to achieve the initial inoculum for the thermophilic hydrolysis essays.

For the hydrolysis tests, one stainless steel reactor of 10.0 L was inoculated with 10% of digestate at an OLR of 2.5 Kg VS m⁻³ d⁻¹ of dried silage. Microminerals were added and the pH was adjusted to 6.0 with HCL 1:1. The reactors were purged with nitrogen for 5 minutes and the temperature was kept at 55°C. The reactor was kept at this temperature and continuously stirred for 5 days to increase the hydrolytic bacteria. After, the solid particles for the reactor were separated using a 2 mm sieve. The remaining liquid was used as inoculum for all the reactors.

All the 12 glass reactors were inoculated with the hydrolytic broth at different conditions of OLR and HRT. For the two of stainless steels reactors, the 6 and 4 day HRT were started simultaneously at 2.5 Kg VS m⁻³ d⁻¹. Once the three HRT for the hydrolysis experiments were completed for the 4 day HRT, the HRT was changed to 2 day at the same OLR.
After 7 days of running the glass reactors, the OLR of 5 and 6 Kg VS m⁻³ d⁻¹ at 10 and 6 day HRT were stopped as they become a very thick broth, making them unable to stir. The experiments at these conditions were aborted and results are not shown.

2.4. Biological Methane Potential

Small BMP tests were performed in 125 ml serum bottles with 70 ml working volume. The ratio of substrate to inoculum was 1:2 with 10 gVS total in the bottle. Microminerals and macrominerals were added. NaHCO₃ was added as a buffer at 3 g L⁻¹. The bottles were purged with Nitrogen for 3 minutes and sealed with butyl rubber stoppers and aluminium crimp seals. The bottles were incubated in an incubator shaker at 38°C and 120 rpm. The biogas produced was measured using a pressure sensor and methane content was measured by GC as described in next section. All the samples were carried out in triplicates.

2.5. Analytical methods

Total solids (TS) and volatile solids (VS) were determined according to standard methods APHA [11]. Soluble COD (sCOD) was analysed using a HACH heating block and a Hach DR/2700 spectrophotometer. pH was monitored using a Jenaway 350 pH meter. VFA was determined by gas chromatography (Perkin Elmer Autosystem XL, PSS injector, FID detector, gas column ZB-FFAP 30 m x 0.32 mm). Helium was used as a carrier gas. Injector and detector temperatures were 230°C, 255°C respectively; a ramp from 100 to 250°C was used in the oven. The methane composition was determined using the same system and same column used for VFA determination with manual injections using a gas tight syringe being the injector, oven and detector at 200 °C, 170 °C and 225 °C respectively.

3. Results and Discussion

3.1. Effect of Volatile Solids (VS) Destruction

Table 1 shows the percentage of VS destruction. The overall VS destruction varies from 19% to 45%. From these experiments, it is difficult to find which operational parameters (OLR, HRT) are the best for the destruction of VS, as both affect VS contents simultaneously [2,3,9]. The percentage of VS destruction varies within the range of 20 to 45.

<table>
<thead>
<tr>
<th>HRT (days)</th>
<th>OLR (Kg VS m⁻³ d⁻¹)</th>
<th>6.5</th>
<th>5</th>
<th>2.5</th>
<th>2.5, 9 L</th>
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</thead>
<tbody>
<tr>
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<td>22.93</td>
<td>28.56</td>
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<td>29.29</td>
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<td></td>
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</tr>
<tr>
<td>10</td>
<td></td>
<td>43.33</td>
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3.2. Effect of pH, SCOD and VFA production

The pH of the different effluents in the hydrolytic processes (Figure 1) varied between 5 and 6 for almost all the conditions evaluated except for the hydrolytic process carried out in the stainless steel reactor at OLR of 2.5 Kg VS m⁻³ d⁻¹ for 2 day HRT. The optimum pH for the hydrolysis of grass silage is within the range of that different authors had reported in the literature [2,5,7,9,12]. The pH decreased with the increase of the OLR, but the HRT had not
significant effect on the pH variation when the OLR was kept constant. These results are in line with the observation of Nizami et al. [2,9].

![Graph](image1.png)

Figure 1. pH of grass silage effluent in hydrolysis pretreatment of grass silage

The VFA production increased when both the HRT and the OLR increased as shown in figure 2. This trend is in agreement with the results obtained by De la Rubia [5]. Table 2 shows the VFA concentration and composition in percentage. The highest concentrations of VFA (1530 mg L\(^{-1}\)) were obtained for OLR of 2.5 Kg VS m\(^{-3}\) d\(^{-1}\) at 10 day HRT. This was followed by OLR of 2.5, 5 and 6.5 Kg VS m\(^{-3}\) d\(^{-1}\) at 6 and 4 day HRT respectively with an average value of VFA 1109 mg L\(^{-1}\).

Table 2. VFA production and composition

<table>
<thead>
<tr>
<th>OLR (Kg VS m(^{-3}) d(^{-1}))</th>
<th>HRT (days)</th>
<th>VFA mg L(^{-1})</th>
<th>Acetic acid (%)</th>
<th>Propionic Acid(%)</th>
<th>Isobuturic Acid(%)</th>
<th>Butyric Acid (%)</th>
<th>Isovaleric Acid(%)</th>
<th>n-Valeric Acid (%)</th>
<th>Isocaproic Acid (%)</th>
<th>n-caproic Acid (%)</th>
<th>Heptanoic Acid (%)</th>
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<td>2.5</td>
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<td>216.83</td>
<td>70</td>
<td>9</td>
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<td>35</td>
<td>2</td>
<td>1</td>
<td>3</td>
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<td>412.54</td>
<td>69</td>
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<td>6</td>
<td>2</td>
<td>3</td>
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<td>6</td>
<td>1</td>
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<td>1</td>
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<td>0</td>
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<tr>
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<td>13</td>
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<td>28</td>
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<td>2</td>
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<td>828.29</td>
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<td>14</td>
<td>2</td>
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<td>2.5, 9.0 L</td>
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<td>1149.85</td>
<td>51</td>
<td>11</td>
<td>2</td>
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<td>3</td>
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</table>

The predominant VFA produced was acetic acid, varying from 70 to 38%. This was followed by butyric acid (varying from 3 to 35%) and propionic acid (varying from 5 to 18%). The others VFA were within the range of 0 – 4%. At an OLR of 6.5 Kg VS m\(^{-3}\) d\(^{-1}\) with 4 and 2 day HRT, the acetic acid was dominant (88 and 69 % respectively) and butyric acid was at the minimum (3 and 6 % respectively).

The sCOD has increased when both OLR and HRT increase (Figure 5). The sCOD was doubled when the HRT increased at OLR of 5 and 6 Kg VS m\(^{-3}\) d\(^{-1}\). An increase of 77% in sCOD was observed at OLR of 2.5 Kg VS m\(^{-3}\) d\(^{-1}\). This trend of increase in sCOD during the hydrolysis of grass silage is also observed by Nizami et al. [2] in the same patterns.
3.4. Methane Yield (BMP)

The BMP test provides an indication of what is the maximum CH₄ a substrate can generate in AD process. All the conditions evaluated for thermophilic hydrolysis had increased the CH₄ production. Figure 7 shows the BMP test values obtained at different OLR and HRT after the hydrolysis and digestion of grass silage as substrate. The BMP value for the dried silage without hydrolysis pretreatment was 0.225 m³ CH₄ g⁻¹ VS, (STP). The BMP for the hydrolysis pretreatment at the different OLRs and HRTs were between the range of 0.286 to 0.400 m³ CH₄ (STP) gVS⁻¹. One of the highest BMP values were obtained at OLR of 5 Kg VS m⁻³ d⁻¹ at 2 day HRT. The BMP value was 0.391 CH₄ (STP) gVS⁻¹, which was 73% increase when comparing with the BMP of the untreated silage. The BMP value increased 77% for the OLR of 6.5 Kg VS m⁻³ d⁻¹ OLR and 2 day HRT (0.400 CH₄(STP) gVS⁻¹). The shortest HRT (2 days) gave the highest values for BMP in agreement with previous studies as described by Pakarinen [13], except for the operational conditions when the reactor was operated at OLR of 2 Kg VS m⁻³ d⁻¹ for 10 day HRT.

4. Conclusion

The maximum BMP obtained after the thermophilic hydrolysis of grass silage was observed at an OLR of 2.5 and 5 Kg VS m⁻³ d⁻¹ at 2 day HRT. The VFA was one of the most important parameters, when the percentage of acetic acid was between 60-70% to obtain the highest methane yield. A range of methane production from 0.22 to 0.400 m³ CH₄ (STP) gVS⁻¹ was obtained from BMP assays. In a two stage AD process for methane production, having a first hydrolytic stage when using grass silage as a substrate in AD process is valuable.

Acknowledgments

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5. References


