CO-DIGESTION OF HOG MANURE WITH GLYCEROL TO BOOST BIOGAS AND METHANE PRODUCTION

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ABSTRACT. The use of off-farm materials as amendments in anaerobic digestion of manure is an option that is being explored more extensively due to the benefits of boosting methane production and making the process more economical for the farmer. The addition of varying amounts of glycerol, which is a by-product in the biodiesel industry, was used as an amendment to anaerobic digestion of hog manure in bench-scale tests. The use of 2% glycerol produced the greatest amount of methane and biogas, while the addition of 4% glycerol resulted in an overloading of chemical oxygen demand (COD) and digester failure. The addition of 1% glycerol doubled the methane and biogas production, and there appeared to be no detrimental effects of using crude, industrial-based glycerol compared to pure, chemical-grade glycerol.

Keywords. Anaerobic digestion, Biogas, Glycerol, Hog manure, Methane.

With concerns over the depletion of fossil fuels and the emission of greenhouse gases (GHG), which contribute to global climate change, extensive research is being conducted to address these environmental problems through the utilization of farm and industrial wastes. One particular process, which has been used for many years but generally under-utilized in Manitoba and Canada, is anaerobic digestion (AD) of animal wastes on a farm scale. Anaerobic digestion is simply the process of converting organic matter into biogas in the absence of oxygen through the activity of microorganisms (Metcalfe and Eddy, 2003). This option addresses both concerns by producing renewable fuel and reducing GHG emissions, as well as supplying farmers with high-quality fertilizer.

In an effort to boost biogas and methane yields, and make the process more economical, co-digestion of agricultural and municipal wastes with different amendments has been explored (Yadavik et al., 2004; Angelidaki and Ahring, 1997; Chung et al., 2007). The use of co-substrates can have many advantages in anaerobic digestion because co-substrates can supply nutrients that may be deficient and that have an overall positive synergistic effect in the digestion medium, leading to enhanced yields. The co-substrates used are often offsite waste materials, which have little other use. Some examples include the use of cattle or poultry manure, food waste, organic municipal solid waste, corn silage, and slaughterhouse waste (Mladenovska et al., 2003; Kaparaju and Rintala, 2005; Callaghan et al., 1999). At the wastewater treatment facility in Millbrae, California, the use of grease trap waste in municipal waste increased biogas production by 150%, and additional revenue was received from tipping fees (Chung et al., 2007).

The largest contributor of FOG (fats-oils-grease) wastes are restaurants, food preparation facilities, and industrial processing plants, which often release these wastes directly into the sewers. This FOG, when properly digested, has been proven to produce methane at higher rates than other organic matter, as it is able to enhance the degradation of other organic feedstocks in the digester (Bailey, 2007). At the City of Riverside WWTP in California, 20% to 30% additions of FOG to the digester sludge resulted in almost doubling the biogas production, which led to significant energy savings (Bailey, 2007).

A waste product similar to grease that could be used in anaerobic digestion applications is glycerol (or glycerine). As is the case with FOG, glycerol is a high COD content co-substrate that can be used in conjunction with lower organic content feedstocks, such as municipal biosolids or animal manure, in an effort to boost biogas yields. Glycerol, a readily biodegradable sugar alcohol, is a byproduct of biodiesel production and is of particular interest in the province of Manitoba, due to the anticipated increase in the biodiesel industry and the associated waste products (Biodiesel Advisory Council, 2005).

There is limited research on the use of glycerol or glycerine oils in anaerobic digesters. In one research study (Mladenovska et al., 2003) involving a mixture of cattle manure with 2% glycerol trioleate (GTA, a glycerine oil), significantly better specific methane yields (224 to 382 mL CH4 g-1 VS d-1) and a higher removal of organic matter (37% to 51%) were observed when compared to a digester operated solely with manure. The reactor with mixed waste (lipids and manure) also exhibited a microbial community with higher densities and higher numbers of methanogenic microorganisms (Mladenovska et al., 2003). Using batch digesters, Amon et al. (2006) showed that with the addition of glycerol...
to hog manure in varying amounts, a consistent increase in methane production could be observed along with a co-fermentation effect, which was defined as the additional methane yield observed beyond that of the combined yields of both substrates if digested separately. This co-fermentation effect was highest with glycerol additions of 3% to 6% in hog manure that had a total solids content of approximately 4%. Amon et al. (2006) also suggested that the addition of glycerol should not exceed 6% by volume to ensure stable operation. For co-digestion of manure with glycerol in semi-continuous lab digesters, Holm-Nielsen et al. (2008) showed that a loading of 3% (vol) glycerol was fairly easy to manage and gave increasing biogas yields. However, when the glycerol concentration exceeded 5 to 7 g L⁻¹ in the digester, methane was significantly reduced from the organic overloading. All of the above studies were conducted with laboratory-grade glycerol as co-substrate.

This research study focused on the addition of varying amounts of glycerol to hog manure in a continuous-feed digester system in an attempt to boost biogas and methane production. A variety of glycerol-to-manure feeding ratios were investigated in order to determine suitable feeding regimes and evaluate thresholds for carbon overloading. Both purified, chemical-grade glycerol and crude, industrial-grade glycerol, obtained from a biodiesel production process, were tested to assess the impact of impurities in the crude glycerol on digestion efficiency.

METHODS

Four lab-scale, complete-mix anaerobic digesters were operated at 35°C in a constant-temperature environmental chamber. Dilute hog manure and glycerol were fed to the reactors at a rate of 200 mL d⁻¹, resulting in a hydraulic retention time of 17.5 days. The working volume of each digester was 3.5 L with an additional 0.5 L of headspace (fig. 1). The raw hog manure was obtained from Cook Feeders farm, a 6,000-head finishing hog operation located in Teulon, Manitoba. This manure was delivered to the University of Manitoba, where it was screened through a 1.2 mm sieve to remove any large particles that might cause clogging in the tubing and restrict mixing. The manure was also diluted with varying amounts of water to equalize the organic loading to the reactors from the manure portion of the feed over the operational period. The average total solids content of the manure was approximately 1%, total COD concentration was 16.7 g COD L⁻¹, pH was 7.6, alkalinity was 6515 mg CaCO₃ L⁻¹, and ammonia concentration was 1240 mg N L⁻¹. The biogas produced was sampled from the digester headspace for quality analysis and collected in gas collection bottles for volume determination using liquid displacement.

The four digesters were fed semi-continuously (once a day). The control digester was fed only hog manure, while the other three digesters were fed mixtures of manure with 1%, 2%, and 4% glycerol by weight, which was equivalent to 1.7 to 1.8, 2.3, and 4.3 times the COD load, respectively. One of the three treatment digesters was used in a second run at a later time, for a total of five runs. The glycerol used was laboratory grade (99% pure), as well as crude glycerol obtained from a biodiesel production unit, which contained residual salts (10 g sodium L⁻¹) and methanol (approximately 1%). The reactors were operated for 57 to 88 days (runs varied in length due to reactor failure or instability) and were mixed at all times.

The digester effluent was characterized for alkalinity, pH, total solids (TS), and volatile solids (VS) on a weekly basis according to standard methods (APHA, 2005). The biogas production rates were recorded daily, and gas samples were taken from the reactor headspace on a weekly basis. Gas composition analysis, as well as volatile fatty acid (VFA, C2 to C8) analysis, was done using gas chromatography (Varian CP8410, GC) with a flame ionization detector. Total COD was measured with a modification of the standard methods (APHA, 2005), using Hach method 8000 digestion vials.

RESULTS AND DISCUSSION

The results shown below are average values from the digesters, once they were determined to be operating at a steady state as indicated by a constant methane yield and low VFA-to-alkalinity ratio (below 0.2), as described by Schaef er and Sung (2008). The lack of replicate digesters for each feedstock option is a limitation of this study. However, it was not possible to run a larger number of digesters in continuous-feed mode due to logistical reasons. Before adding glycerol to the reactors, stable and similar gas production was observed in all four reactors. The acclimation and stabilization phase lasted approximately two months. Once glycerol was added to the three treatment reactors at varying levels, stable gas production was observed in the 1% crude glycerol digester after 8 days of glycerol feeding. The 1% pure glycerol digester was operating steadily after approximately 20 days, while the 2% and 4% pure glycerol digesters never achieved steady gas production. The feed, effluent, and gas characteristics of all five digester runs are summarized in table 1.

SHOCK LOADING PERFORMANCE

Three digesters were exposed to sudden increases of organic loading (from a control of 1.05 g COD L⁻¹ d⁻¹ to 1.8, 2.46, 4.11 g COD L⁻¹ d⁻¹ for the 1%, 2%, and 4% glycerol-amended reactors, respectively), which were considered shock loads. As these higher loads were not reached by slow and stepwise increases but by sudden changes to the feed, the term “shock load” was deemed suitable. The two digesters that were fed 2% and 4% glycerol amendments showed an almost immediate doubling of biogas and methane
Table 1. Characteristics of the feed, effluent and gas for all five anaerobic digester runs.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>COD Loading (g L(^{-1}) d(^{-1}))</th>
<th>pH</th>
<th>Alkalinity (mg CaCO(_3) L(^{-1}))</th>
<th>Volatile Solids Reduction (%)</th>
<th>COD Removal (%)</th>
<th>CH(_4) (%)</th>
<th>CH(_4) Yield (m(^3) CH(_4) kg(^{-1}) COD removed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (manure only)</td>
<td>1.05</td>
<td>7.6</td>
<td>6515</td>
<td>43</td>
<td>61</td>
<td>71</td>
<td>0.4</td>
</tr>
<tr>
<td>1% pure glycerol + manure</td>
<td>1.8</td>
<td>7.4</td>
<td>6408</td>
<td>42</td>
<td>70</td>
<td>63</td>
<td>0.37</td>
</tr>
<tr>
<td>1% crude glycerol + manure</td>
<td>1.96</td>
<td>7.5</td>
<td>6758</td>
<td>48</td>
<td>74</td>
<td>67</td>
<td>0.36</td>
</tr>
<tr>
<td>2% pure glycerol + manure</td>
<td>2.46</td>
<td>7.3</td>
<td>5610</td>
<td>67</td>
<td>72</td>
<td>66</td>
<td>0.39</td>
</tr>
<tr>
<td>4% pure glycerol + manure</td>
<td>4.11 [a]</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

[a] NA = not available due to digester instability.

production after just 3 days. However, both digesters failed and were not able to reach a steady state (fig. 2). The quick response in gas production was likely due to breakdown of the readily biodegradable soluble COD in the glycerol. However, due to the sustained high COD loading, acid increased, and a substantial pH drop resulted in an unstable system (fig. 3). The 4% glycerol digester exhibited a sharp decline in gas production after approximately 5 days and essentially stopped producing any biogas after 12 days. This corresponded to a steady drop in pH to a low value of 5.66 and an increase in volatile fatty acids (VFAs) to a maximum of over 10,000 mg L\(^{-1}\), an environment unsuitable for methanogenesis (Ros and Zupancic, 2003; Schaefer and Sung, 2008). The feeding of glycerol was stopped, but the bacteria in this digester were not able to recover, and reseeding was required. The 2% glycerol digester showed a slower shock effect, but it also failed to stabilize and began building up high levels of VFAs to a maximum of over 7,000 mg L\(^{-1}\) after approximately 25 days, which corresponded to a sharp reduction in biogas and methane production, at which time glycerol feeding was stopped (fig. 4) and the reactor was allowed to recover on hog manure only. No negative shock loading effect was observed with the 1% glycerol digester, and its gas production remained relatively stable throughout operation (fig. 5).

**DIGESTER RECOVERY**

The digester with the 2% glycerol amendment was allowed to recover after the shock loading by feeding it only hog manure for a period of 45 days, until it had stabilized to control conditions, and then it was fed 2% glycerol again to test the bacterial tolerance to the sustained high COD loading. During the second feeding stage with 2% glycerol, the bacteria in the digester were more resilient, and after 88 days this digester was producing approximately 2.5 times more methane than the control digester and almost 3 times more biogas. Once again VFAs built up in the digester initially, but only to a maximum of approximately 4,000 mg L\(^{-1}\) after 25 days, before they began to decrease as they were consumed and converted to biogas. Gas production in this digester showed a steady increase throughout its operation until it stabilized, indicating that the bacteria continued to convert the excess VFAs into biogas and methane, as shown in figure 4, while the methane content in the biogas also increased over time from 49% to 66%. This digester was operated until steady state was reached, as indicated by the constant methane yield and low (below 0.2) VFA-to-alkalinity ratio, as described by Schaefer and Sung (2008). The performance of this digester suggests that the population of the glycerol-utilizing bacteria increased during the first run and were out-competing the slower-growing heterotrophic bacteria in the second run.

**PURE VS. CRUDE GLYCEROL**

A comparison experiment was done with digesters fed manure with 1% pure glycerol and 1% crude glycerol to determine whether impurities in the crude glycerol, such as methanol and salts, have any detrimental effect on biogas and methane production. The feed COD for the 1% crude glycerol digester was slightly higher than for the 1% pure
glycerol digester due to some residual methanol (a process chemical in biodiesel production) in the crude glycerol. During the operation period of 57 days, both digesters behaved similarly overall, with the crude glycerol digester showing slightly higher methane content, COD removal, and volatile solids removal. Biogas and methane production were virtually the same, with both digesters producing approximately double the amount of the control digester with manure alone (fig. 5). Therefore, the use of crude glycerol as an amendment did not exhibit any detrimental effects on digester performance.

**Biogas and Methane Production**

The biogas production followed a trend similar to that of methane production in the 1% glycerol digesters, which both produced approximately double the biogas of the control digester with manure alone. In the 2% glycerol digester, methane production was slightly lower than biogas production, due to the lower methane content in the biogas. The methane yield was quite similar among all four digesters, ranging between 0.36 and 0.40 m$^3$ CH$_4$ kg$^{-1}$ COD removed (fig. 6). The error bars in figure 6 represent the standard deviations of the average methane yields observed in each reactor over the steady-state operational period. No statistically significant differences were observed between the reactors over the time of operation. The observed methane yields and biogas composition were generally in agreement with previous studies. A study by Qatibi et al. (1991) revealed that anaerobic degradation of glycerol by a mixed culture led to the formation of 1,3-propanediol prior to propionate and acetate formation. In that study, the propionate accumulated to higher levels than the acetate and degraded more slowly.

The addition of glycerol, despite increasing amount of overall biogas and methane produced, actually resulted in a small reduction of methane content in the biogas, while increasing the carbon dioxide content. The methane content in the biogas of the control digester was the highest at 71% CH$_4$, but it remained relatively high in all three glycerol treatments and ranged from 63% CH$_4$ in the 1% pure glycerol digester to 67% CH$_4$ in the 1% crude glycerol digester. The 2% glycerol reactor had a surprisingly high CH$_4$ content of 66%, while the majority of the remaining gas produced was carbon dioxide.

The decrease in methane production corresponded to an increase in overall VFA production and more specifically the production of propionic acid, while a decrease in propionic acid led to higher methane content, as shown in figure 7. This increase in VFA production and buildup of propionic acid is an indication of low metabolic activity and overall system imbalance (Ahiring et al., 1995; Pind et al., 2003). Ahiring et al. (1995) reported that the relative changes in VFA concentrations are a better indication of imbalance than their absolute values. When looking at individual VFAs, it is important to understand that the two-carbon acetate is one of the simplest carboxylic acids, derived from the degradation of the three-carbon propionate, which comes from the degradation of higher-carbon fatty acids (C4 to C7). This is important because increases in acetate in an anaerobic digester have been shown to increase metabolic activity and methane production, and degradation of propionate is the slowest of all VFAs. A buildup of propionate can be a good indication of low metabolic activity and slow stabilization (Pind et al., 2003).
CONCLUSIONS

The use of glycerol as an amendment to anaerobic digestion of hog manure has proven to increase both biogas and methane production because glycerol has a high amount of readily biodegradable soluble COD, which can be easily consumed by anaerobic bacteria.

It was shown that the microbial population in a digester could recover and actually develop a tolerance for the high COD loading of a 2% glycerol amendment. The performance of this digester suggests that incremental glycerol additions may provide a stronger and healthier population than shock loading the system, which can lead to instability and digester failure.

Compared to pure glycerol, the addition of crude glycerol from a biodiesel production unit did not seem to have any detrimental effects on digester performance, despite containing additional COD from residual contaminants, such as methanol and salts. The overall behavior was very similar to that of the digester fed with an equal amount of pure glycerol, which indicates that crude glycerol from biodiesel production could be used as a co-substrate in a digester without any additional refining.

The methane yield was similar among the control, 1% glycerol (pure and crude), and 2% glycerol digesters, ranging from 0.40 m³ CH₄ kg⁻¹ COD removed in the control to 0.36 m³ CH₄ kg⁻¹ COD removed in the 1% crude glycerol digester, indicating a stable and healthy bacterial culture that is able to utilize the high COD glycerol feed.

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REFERENCES


