Biochemical Methane Potential of Municipal Solid Waste and Biosolids

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OBJECTIVE:

The objective of this research was to quantify the ultimate methane potential of different organic waste fractions comprising typical U.S. municipal solid waste (MSW), as well as the methane potential of wastewater and manure digester biosolids. This research will supplement a current experimental program designed to investigate the effect of co-disposal of MSW with three different potential anaerobic inocula (i.e., wastewater treatment biosolids, manure digester biosolids, and MSW leachate) on methane production, waste stabilization, and microbial community dynamics. The coupling of these two experimental programs will enhance our understanding of the interactions between the biological, chemical, and physical mechanisms of MSW decomposition and methane generation in bioreactor landfills.
INTRODUCTION

The landfill industry is currently in transition from the conventional landfill, where municipal solid waste (MSW) biodegradation is minimized due to limited moisture addition, to the bioreactor landfill, where MSW biodegradation is a primary objective. Waste decomposition is optimized through the increase in moisture content, and also through increase in temperature, and/or nutrient/microbial seed addition to the refuse [1]. The most widely used approach is to increase the moisture content through recirculation of leachate or addition of supplemental liquids (e.g., sewage or industrial wastewater). There is considerable interest in developing operational strategies for municipal solid waste (MSW) landfills that accelerate decomposition, enhance gas generation, improve leachate quality, and reduce leachate treatment costs [2–4]. Methane generated during waste decomposition is captured to prevent atmospheric pollution, and can be used as a valuable source of clean-burning alternative energy [1]. Bioaugmentation of MSW by co-disposal of biosolids such as sludge from municipal or agricultural anaerobic digesters is one proposed strategy to improve methane production and energy recovery. Landfilling is also an increasingly attractive alternative disposal route for biosolids in Dane County, Wisconsin. The traditional biosolid disposal method of land application is associated with undesirable excess soil phosphorus accumulation and contributes to eutrophication of surface waters in the region [5].

There is great interest in improving our ability to predict methane production from bioreactor landfills but these efforts are hindered by the highly heterogeneous nature of MSW [6]. The ultimate methane yield or biochemical methane potential (BMP) differs significantly between and within waste fractions (e.g., paper, wood, food waste), which may themselves be heterogeneous groupings of diverse materials [7], [8]. Reported methane yields from bulk MSW can be highly variable due in part to regional and temporal differences in waste composition [9], [10]. Furthermore, waste decomposition in landfills is incomplete with an estimated less than half of the BMP extracted under normal leachate recirculating conditions [7]. Thus, innovative waste management strategies can potentially increase methane production. Co-disposal with biosolids has been suggested to improve methane extraction from MSW by aiding moisture retention in the waste [11], [12]. An enhanced understanding of the effects of waste composition and co-disposal strategy on methane production will ultimately increase our understanding of
biodegradation of MSW in bioreactor landfills and allow better management and prediction of methane yields.

This project aimed to characterize the biochemical methane potential of biosolids from anaerobic digesters. While several studies have reported the BMP of individual waste fractions, the residual methane potential of biosolids varies with source and location. In a separate ongoing investigation these biosolids, from anaerobic digesters treating municipal wastewater and cow manure, will be added to MSW in laboratory scale landfill simulations to determine the effect of co-disposal on methane yield and generation rate. This research determined the ultimate methane generation potential of waste fractions independently under optimized conditions and will now allow calculations of percent of methane potential extracted in the ongoing landfill simulations. Data from these experiments will be used to calculate the percent of methane potential extracted in our simulations and predict the expected contribution of biosolids addition to total methane production in the landfill simulations. The data generated here will aid us in determining whether increased methane yields following biosolids addition are due solely to biodegradation of the added organic material, or if biosolids addition also improves biodegradation of the MSW. The integration of the data from this project into our ongoing research on co-disposal in bioreactor landfills makes this research directly applicable to waste management practice in Wisconsin.

METHODS/PROCEDURE:

*Preparation of Waste Materials*

To determine the methane potential of waste, landfill waste had to be generalized and broken into its major components. Food, yard waste, and paper were identified as the major components of landfill waste contributing to methane generation in Wisconsin [7]. To ensure a homogeneous substrate across all experiments, food waste was simulated as finely ground up dry dog food and yard waste was simulated as finely ground timothy hay. Only particles passing though a 1-mm screen were used for the assay. Paper waste was simulated as finely shredded
office paper. Residual biosolids from anaerobic digesters were collected from two locations: the Madison Municipal Sewerage District Nine Springs Wastewater Treatment Plant, and the Crave Brothers' Farm in Waterloo, Wisconsin.

Volatile Solids Measurements

The volatile solids composition of each waste type was used to determine how much waste should be added to the BMP assay. Volatile solids represent the portion of the waste that has the potential to be converted into methane gas.

Five replicate measurements of volatile solids were made for each form of waste (dog food, grass clippings, paper waste, and biosolids). Five grams of waste in a standard weigh boat were placed into an oven at 110 °C for approximately 12 hours to dry the waste. The mass of total solids was computed by subtracting the mass of the weigh boat from the mass of the weigh boat and dried sample. The dried sample was then combusted in an oven at 550 °C for approximately 2 hours at 30 min intervals until the mass did not change by more than 1%. The mass of non-volatile solids was computed by subtracting the mass of the weigh boat from the mass of the weigh boat and combusted sample. The mass of volatile solids was computed by subtracting the mass of the non volatile solids from the mass of total solids.

Preparation of Anaerobic Mineral Media

To promote bacterial growth during the BMP assay, a suitable media was made to ensure that the only limiting reagent would be a carbon source. This would ensure that the entire mass of the waste would be digested. Anaerobic mineral media (AMM) was made according to the procedure reported by Owens et al. [13]. To make the media the following chemicals were added to 1000mL of de-ionized/purified water: 0.53 g NH₄Cl, 0.07-0.08 g CaCl₂, 0.1 g MgCl-6H₂O, and 0.2735 g KH₂PO₄ and 0.3516 g K₂HPO₄ were added as well to act as a buffer system. Because the protocol called for trace amounts of some elements, the following compounds were added to 1000mL of de-ionized/purified water and left to dissolve overnight: 0.01-g FeCl₂-4H₂O, 0.54-g MnCl₂-4H₂O, 0.05 -g H₃BO₃, 0.05-0.1-g ZnCl₂, 0.05-g CuCl₂, 0.03-g NaMo₄-6H₂O, 0.07-g CoCl₂-6H₂O, 0.04-g NiCl₂-6H₂O, and 0.05-g Na₂SeO₃. This solution was diluted 1000x in the media The pH of the media was adjusted to 7.0 with NaOH since a neutral pH promotes methanogenesis.
For each set of experiments, 10-g of anaerobic digester sludge from the wastewater treatment plant (WWTP) was added to 1-L of the buffered solution to create an inoculum of anaerobic methane producing microorganisms. For the set of experiments assaying the cow manure anaerobic digester sludge, an indicator dye (resazurin) was added to detect oxygen contamination during the course of the experiment.

**Assay Conditions**

250-mL glass serum bottles were used for this experiment. Each waste material was assayed in triplicate, and triplicate controls with no additional waste or biosolids added were also run. Before anything was placed into the bottles, the bottles were rinsed for 30 seconds with Argon gas and capped to remove oxygen. 50-mL of inoculated AMM and 5 g of waste material or biosolids were added quickly to each bottle, minimizing the amount of time that the stopper was off the bottle to limit the introduction of oxygen. The bottles were then stoppered with butyl stoppers and sealed shut with aluminum seals, and rinsed for 30 seconds with Argon gas to flush out any introduced oxygen. Bottles were incubated at 37 C in a temperature-controlled room.

**Measurement of Gas Production**

At intervals of three days the bottles were removed from the temperature controlled room and allowed to come to room temperature before removing gas. The amount of gas produced was measured by inserting a needle connected to a digital manometer and measuring the pressure differential between the sealed assay bottle and the ambient atmosphere. Pressure was then converted to moles of gas using the ideal gas law, with $V_{\text{headspace}}$ equal to 100 mL.

$$\text{number of moles gas} = \frac{P_{\text{measured}} V_{\text{headspace}}}{RT}$$

The moles of gas were then converted to mL of gas at standard temperature and pressure, and the volume of new gas produced found by subtracting the initial volume of the headspace.

$$V_{\text{produced}} = n_{\text{produced}} \left( \frac{RT}{P_{\text{standard}}} \right) - V_{\text{headspace}}$$
The three replicate values were averaged and reported. After measuring the volume of gas produced, the excess pressure was vented by inserting a needle through the rubber stopper so that pressure buildup would not inhibit the experiment.

The total volume of gas that was produced in the assay bottles was measured until the end of the experiment (day 75), for food, yard, paper, and WWTP sludge waste. For the cow manure digester sludge, the volume of gas produced was measured until day 12, after which time no measurable gas was produced during the remainder of the experiment.

**Methane Measurement**

A Shimadzu Gas Chromatograph model GC-8A with a flame ionization detector was used to determine the concentration of methane in the biogas produced during each assay. The machine was calibrated at each use with 1000-ppm standard of methane. Different volumes of gas standard from 500- to 50-ul were used to create a calibration curve to relate integrated peak height to methane mass. Triplicate readings of 100-ul each were taken from the headspace of each assay bottle and the average peak height converted to moles of methane using the standard curve. The mole fraction of methane in each bottle was then multiplied by the total volume of gas produced to give the total volume of methane produced.

**RESULTS:**

**Volatile Solids**

Percent moisture and volatile solids for each of the waste types is given in Table 1, along with volatile solids as a percentage of total solids (VS/TS). The WWTP anaerobic digester sludge had the highest moisture content, and paper the lowest. Volatile solids as a percentage of total solids was lowest in anaerobic digester sludge, reflecting its status as already degraded waste. It was highest in food waste.

| Table 1. Percent moisture content, volatile solids content, and volatile solids (VS) as a percentage of total solids (TS) for each waste source. |  |
Gas Production Volume and Rates

The total volume of gas that was produced in the assay bottles was measured until day 75 when the experiment was ended due to low gas production rate from the anaerobic digester sludge. Gas production rate is shown in Figure 1. The WWTP anaerobic digester sludge and the control, which contained WWTP sludge, proceeded at a similar rate. The manure digester sludge had the highest rate of methane production, but produced methane for a shorter period of time than the WWTP sludge.

<table>
<thead>
<tr>
<th></th>
<th>Moisture</th>
<th>Volatile Solids</th>
<th>VS/TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food Waste</td>
<td>7.5%</td>
<td>83.8%</td>
<td>90.5%</td>
</tr>
<tr>
<td>Yard Waste</td>
<td>9.0%</td>
<td>80.9%</td>
<td>89.0%</td>
</tr>
<tr>
<td>Paper Waste</td>
<td>2.5%</td>
<td>81.0%</td>
<td>83.1%</td>
</tr>
<tr>
<td>WWTP Sludge</td>
<td>91.8%</td>
<td>5.4%</td>
<td>66.7%</td>
</tr>
<tr>
<td>Manure Sludge</td>
<td>69.8%</td>
<td>3.4%</td>
<td>11.3%</td>
</tr>
</tbody>
</table>

Figure 1. Daily rate of methane production as mL methane per dry gram at standard temperature and pressure. Each data point is an average of 3 replicate assays.
Figure 2 shows the cumulative volume of methane produced throughout the length of the experiment. The paper waste and the anaerobic digester sludge produced the most methane, while the food and yard waste produced very little. The control produced more methane gas than the yard waste and food waste.

![Graph showing cumulative volume of methane produced per dry gram of waste during the experiment.](image)

**Figure 2.** Cumulative volume of methane produced per dry gram of waste during of the experiment.

**DISCUSSION:**

The final measurements of biochemical methane potential, BMP, obtained from this study were significantly lower than expected based on previously published studies of yard, food, and paper waste (130, 300, and 217 mL per dry gram, respectively) [7]. This is probably in part because complete waste degradation was not achieved in this experimental setup. At the end of the 75 days the office paper was still visibly intact and recognizable in its original form in the
assay bottles, suggesting it failed to degrade completely. This is also supported by the continued gas production from paper, even at 74 days. However, very little methane was produced from yard or food waste at any point in the experiment, in contrast with published studies showing very high methane potential for food waste. Though we are unsure of the reason for the low methane production, it is likely that the assays became too acidified for methanogenesis to occur. Overproduction of acid is a well-documented problem in anaerobic waste degrading systems [14], though we were unable to confirm this hypothesis with measurements of pH as the BMP reactions were conducted in sealed containers.

We were able to obtain values for the BMP of anaerobic digester sludge from digesters treating both cow manure and wastewater. The final yield of methane for manure sludge was $5.13 \pm 1.81 \text{ mL/dry gram}$, and for wastewater sludge was $8.5 \pm 1.34 \text{ mL/dry gram}$. The wastewater sludge had a higher volatile solids content and therefore was expected to produce more methane. However, the control assays, with no source of degradable waste other than the inoculated wastewater sludge in the mineral media, had higher methane production than any waste source other than paper, with a final yield of $12.1 \pm 2.54 \text{ mL/dry gram}$. It is unclear why the control assays had slightly higher methane yield than the wastewater assays when the waste source was identical, but it may be that the assays operated more efficiently at a lower loading rate.

CONCLUSIONS

Anaerobic digester sludge from digesters treating both cow manure and wastewater treatment plant sludge have residual methane potential. Both sources contain viable microorganisms capable of converting varied waste sources to methane. The measured methane potential of anaerobic digester sludge was low relative to the published methane potentials of other waste sources such as paper. Therefore these waste sources may serve as sources of viable microorganisms for degradation in Wisconsin landfills, without increasing the gas production beyond the capacity of current landfill infrastructure to manage. Furthermore, mixture of
biosolids with MSW could be a desirable alternative to land application, mitigating associated problems of nutrient run-off.

BIBLIOGRAPHY: