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Methane and hydrogen sulfide production during co-digestion of forage radish and dairy manure

Ashley J. Belle [a], Stephanie Lansing [a,*], Walter Mulbry [b], Ray R. Weil [a]

[a] Department of Environmental Science and Technology, University of Maryland, 1449 Animal Science/Ag Engineering Building, College Park, MD 20742, USA

[b] United States Department of Agriculture-Agricultural Research Service, Sustainable Agricultural Systems Laboratory, Beltsville, MD 20705, USA

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ABSTRACT

Forage radish, a winter cover crop, was investigated as a co-substrate to increase biogas production from dairy manure-based anaerobic digestion. Batch digesters (300 cm^3) were operated under mesophilic conditions during two experiments (BMP1; BMP2). In BMP1, the effect of co-digesting radish and manure on CH_4 and H_2S production was determined by increasing the mass fraction of fresh above-ground radish in the manure-based co-digestion mixture from 0 to 100%. Results showed that forage radish had 1.5-fold higher CH_4 potential than dairy manure on a volatile solids basis. While no synergistic effect on CH_4 production resulted from co-digestion, increasing the radish fraction in the co-digestion mixture significantly increased CH_4 production. Initial H_2S production increased as the radish fraction increased, but the sulfur-containing compounds were rapidly utilized, resulting in all treatments having similar H_2S concentrations (0.10–0.14%) and higher CH_4 content (48–70%) in the biogas over time. The 100% radish digester had the highest specific CH_4 yield (372 ± 12 L kg^{-1} VS). The co-digestion mixture containing 40% radish had a lower specific CH_4 yield (345 ± 2 L kg^{-1} VS) but also showed significantly less H_2S production at start-up and high quality biogas (58% CH_4). Results from BMP2 showed that the radish harvest date (October versus December) did not significantly influence radish C:N mass ratios or CH_4 production during co-digestion with dairy manure. These results suggest that dairy farmers could utilize forage radish, a readily available substrate that does not compete with food supply, to increase CH_4 production of manure digesters in the fall/winter.

1. Introduction

The economics of manure-only digestion are not always favorable due to the low methane (CH_4) yield of manure compared to other organic substrates [1–3]. However, co-digestion of manure with additional substrates can increase CH_4 production if appropriate substrate co-digestion ratios are determined, as the composition of each substrate can greatly vary in characteristics such as alkalinity, pH, organic content,

* Corresponding author. Tel.: +1 301 405 1197; fax: +1 301 314 9023.
E-mail addresses: abelle@umd.edu (A.J. Belle), slansing@umd.edu (S. Lansing), walter.mulbry@ars.usda.gov (W. Mulbry), rweil@umd.edu (R.R. Weil).
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nutrient composition, and microbial population [4–6]. Bah et al. [7] demonstrated that as the ratio of palm pressed fiber to cattle manure increased from 1:3 to 3:1 (VS basis), CH_4 yield significantly increased, whereas Zhang et al. [8] showed that the CH_4 yield decreased as the ratio of food waste to cattle manure increased from 2:1 to 4:1 (VS basis).

Co-digestion has also been shown to have a synergistic effect on CH_4 production. A synergistic effect results in increased CH_4 production from the substrates beyond what is achieved from digestion of each individual component [5,9]. A synergistic effect was observed when co-digesting equal mass fractions of municipal solid waste, slaughterhouse waste, manure, and various crops. Due to the mixture satisfying more of the nutritional demands of the microbial community, co-digestion increased CH_4 production by 31% compared to the CH_4 production value of each individual fraction [5].

The chemical composition of plant tissue commonly varies over time as the plant matures, which can potentially affect the CH_4 yield when utilizing plant material as co-digestion substrate. Masse et al. [10] determined that the CH_4 yield of switchgrass decreased with advancing stages of development and Ragaglini et al. [11] found that the juvenile crop stages of giant reed had the highest CH_4 production. In contrast, Bruni et al. [12] found that fresh maize at late harvest had the highest CH_4 yield. These inconsistent results highlight the need for further research on the effect of harvest time on digestion efficiency and led Lehtomaki et al. [13] to conclude that the effect of harvest time on anaerobic digestion (AD) was crop specific.

This study investigated coupling AD technology with a new forage radish cover cropping system in order to increase CH_4 production of dairy manure digesters by providing a readily available co-digestion substrate that does not compete with food production. Review of the literature revealed that the specific CH_4 potential of radish varied greatly (237–450 L kg^{-1} VS) depending on plant variety, soil characteristics, climatic conditions, the portion of the plant digested, and pretreatment methods [14–18]. To our knowledge, radish co-digestion studies are limited to one report utilizing radish fodder (whole plant) and pig slurry at one substrate mixture ratio [19].

The above-ground biomass of forage radish cover crops was harvested for co-digestion substrate, allowing for the nitrogen captured by the below-ground roots to remain in the field for the subsequent corn crop upon decay [20,21]. Utilizing forage radish, a cover crop that would otherwise winter-kill, could potentially enable dairy farmers to produce additional renewable energy without losing benefits of the cover crop such as compaction alleviation and weed suppression [22–24]. Additionally, as forage radish is a sulfur-rich crop, the transformation of sulfur-containing compounds in the radish to hydrogen sulfide (H_2S) in the produced biogas was determined as H_2S can corrode biogas utilization systems and have an inhibitory effect on CH_4 production. The specific research objectives were to: (1) determine the effect of varying the co-digestion ratio of dairy manure and forage radish on CH_4 production and H_2S concentration, (2) determine whether inclusion of forage radish to dairy manure has a synergistic effect on CH_4 production, and (3) determine the effect of forage radish harvest date on CH_4 production.

2. Materials and methods

2.1. *Feedstocks*

Forage radish cover crops (*Raphanus sativus* var. *longipinnatus*) and dairy manure (both scraped manure and the liquid fraction of solids-separated manure) were used as digestion substrates. The above-ground biomass of the forage radish cover crop was harvested from a USDA facility located in Beltsville, MD (39.03°, −76.89°). Planting of the radish cover crop occurred in August immediately after corn silage harvesting. The radish was harvested by hand prior to winter-kill from randomized 1 m^2 quadrants. A stainless steel knife was used to harvest the above-ground biomass, which consisted of the leafy shoots plus a small portion of the fleshy root that extended above the soil surface. Each radish was cut approximately 3–5 cm from the soil surface and frozen in heavy-duty plastic bags until use. After thawing, a food processor was used to create a radish pulp, which reduced the radish particle size to less than 3 cm in order to simulate the mechanical harvesting of radish utilizing a rotary mower, forage chopper, and industrial vertical cutter [25].

Dairy manure was obtained from the 120-cow USDA research dairy facility. The dairy manure was scraped and stored in a manure pit prior to solids separation with a FAN separator, which removes roughly 80% of the solids. The liquid fraction of the separated manure is treated in a mesophilic (25–35 °C; 298–308 K) complete-mix anaerobic digester (540 m^3). Inoculum from this digester was obtained from a sampling port located inside the digester and was utilized to accelerate biogas production in the batch studies.

2.2. *BMP1: co-digestion study experimental design*

Biochemical methane potential (BMP) assays were conducted to determine the CH_4 potential of each substrate individually and during co-digestion at varying ratios. The BMP assay determines the relative biodegradability of an organic material by a consortium of anaerobic microbes under batch conditions. BMP1 assays were based on a modified method of Moody et al. [26] using 21 glass serum bottles (300 cm^3), with three replications of seven treatment groups: manure only (0% radish), radish only (100% radish), and co-digestion mixtures containing radish and dairy manure (the liquid fraction of solids-separated manure) with 20, 40, 50, 60, and 80% radish addition. All substrates were added on a wet mass fraction basis, with an equal quantity of substrate in each bottle. BMP1 was conducted for 30-days, the time period in which biogas production had largely ceased, with daily biogas production contributing <1% of the cumulative biogas production.

An equal quantity of inoculum was added to each BMP bottle, resulting in the inoculum to substrate ratios (ISR) ranging from 3.3:1–1.5:1 by VS, which was similar to Raposo et al. [27] where the ISR ranged from 3:1–1:1 by VS and showed little variability in the CH_4 yield coefficient. Three additional BMP bottles containing inoculum-only served as controls. The inoculum had an average pH of 7.53 and total solids (TS) and volatile solids (VS) concentrations of 19.4 and 11.9 g kg^{-1}, respectively. Nutrient media was not utilized as dairy manure