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Research paper

Validation of a simple gravimetric method for measuring biogas production in laboratory experiments

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ABSTRACT

This work presents a gravimetric method for measuring biogas or methane production from anaerobic reactors, based on measurement of reactor mass loss. Results are most sensitive to error in biogas methane content, and less so to temperature and pressure. To evaluate the method, we applied it and volumetric methods to 133 laboratory-scale batch and semi-continuous reactors, ranging in size from 37 g to 8.0 kg of reacting mass. For most observations, the relative difference between the two methods was <10% when the "true" biogas composition was used in calculations. Small systematic differences observed in some cases were probably due to error in estimates of biogas pressure, temperature, and composition, as well as biogas leakage. Based on theory and observation, it is reasonable to expect relative accuracy better than 15% of the true value.

1. Introduction

Existing methods for measuring biogas production from laboratory-scale anaerobic reactors are based on direct measurement of biogas volume or else pressure accumulation [1]. While these methods are technically simple, they are labor-intensive unless automated equipment is used, and automated systems are expensive. In this paper we describe a simpler approach based on mass changes in laboratory-scale reactors. The method is an extension of the methods presented by Richards et al. [2]. A similar gravimetric method has been used for measuring ethanol production by yeast by determining CO_2 production from mass loss, and from this, ethanol production based on stoichiometry [3,4].

2. Methods

2.1. The gravimetric method

The mass of a reactor is determined before and after any period of biogas production, during which time biogas is removed manually or through, e.g., a check valve. The standardized volumes of biogas (V_b, dm^3) and CH_4 (V_{CH_4}, dm^3) lost are calculated from mass loss and estimates of dry biogas density and its water content in six steps, listed below. Mass loss (Δm, g), mole fraction of CH_4 in biogas (x_{CH_4}, normalized so $x_{CH_4} + x_{CO_2}$ =unity), and biogas temperature (T, K) and pressure (P_b, kPa) must be measured or approximated.

1. Calculate biogas molar mass from mole fractions and molar masses of CH_4 and CO_2 (g mol^{-1}):

$$M_b = 16.04x_{CH_4} + 44.01(1 - x_{CH_4})$$

2. From this, calculate density of dry biogas (g dm^{-3}) using a molar volume of 22.3 dm^3 mol^{-1} (at the standard conditions of 273.15 K and 101.325 kPa):

$$d_b = M_b/22.3$$

3. Calculate the saturated vapor pressure of water (kPa) at T with the Antoine equation:

$$\log_{10}P_{H_2O} = 8.20963 - 2354.731/(T + 7.559)$$

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4. With P_{H_2O}, calculate the mass of water removed in biogas ($g\ dm^{-3}$):

$$m_{H_2O} = 18.02P_{H_2O}/(P_b - P_{H_2O}) \cdot 1/22.3$$

5. Calculate standardized biogas volume (dm^3) from Δm:

$$V_b = \Delta m/(d_b + m_{H_2O})$$

6. And calculate production of CH_4 (dm^3):

$$V_{CH_4} = x_{CH_4} V_b$$

These equations are described in detail in the supplementary material, and have been implemented in the new R package "biogas" [5], with which all six steps can be carried out using the function "mass2vol".

2.2. Validation of the gravimetric method

We compared the gravimetric method to conventional volumetric approaches using 111 batch reactors and 22 semi-continuous reactors.

2.2.1. Batch reactors

Batch reactors were 100 cm^3, 500 cm^3, or 1 dm^3 glass serum bottles, with 37–750 g reacting mass. Substrate was pig manure; a mix of pig manure, slaughterhouse, and food waste; municipal wastewater sludge; digestate from a full-scale biogas plant; or cellulose. Inoculum was from two full-scale digesters. Details can be found in the supplementary material. Bottles were sealed with a butyl septum and screw cap, and flushed with dry N_2 for at least 3 volume exchanges of the headspace before incubation. Initial mass was measured after flushing (prior to flushing for 12 bottles), using an electronic balance with a readability of 10 mg (for masses <600 g) or 100 mg for the large reactors. An analytical balance with a readability of 0.1 mg was used for the 100 cm^3 reactors. Bottles were incubated at 37 °C for 30 days (100 cm^3 reactors) or 120–155 days (larger reactors), and biogas volume was measured at room temperature using syringes. For the 84 larger reactors, mass loss was determined only once, directly after removing the final biogas sample. Conversely, mass was measured directly after each biogas removal event from the 27 100 cm^3 reactors—a total of five or six times. Concentrations of CH_4 and CO_2 were determined using a gas chromatograph (GC) with a thermal conductivity detector (TCD) each time gas volume was measured (or once per week when production was high).

2.2.2. Semi-continuous reactors

A single 8.0 kg (reacting mass) dairy manure reactor consisted of a 10 dm^3 plastic carboy sealed with a rubber stopper. Substrate was dairy cattle manure (mass fraction of total solids (TS): 10%, mass fraction of volatile solids (VS) within TS: 85%) once per week, with a hydraulic retention time (HRT) of 30 d. Wasting was done prior to feeding, and both were quantified by mass, using an electronic scale with a readability of 100 mg. The reactor was incubated at 35 °C (±3°) in a temperature-controlled room. Biogas was collected within the room using a 10 dm^3 water displacement system. Concentrations of CH_4 and CO_2 were determined each time volume was measured with a GC equipped with a TCD. Mass loss over the week was based on the difference in two measurements, made just after feeding and sealing the reactor ("initial") and just prior to opening the reactor and wasting ("final").

Richards et al. [2] presented mass loss and biogas production data for 21 semi-continuous laboratory reactors and these data were used here. Substrate was plant biomass (details are presented in the Supplementary material), and feeding and wasting was done once or twice per week. Reactors were 10 dm^3 plastic carboys, containing 5.0 kg reacting mass. They were incubated at 25 °C, 35 °C, or 55 °C in temperature-controlled rooms. Gas was collected in gas bags at room temperature (about 20 °C), which were positioned above the reactors so that condensed water flowed back into the reactors. Biogas volume was measured using a mechanical wet gas meter (calibrated with gas-tight syringes), and concentrations of CH_4 and CO_2 were determined using a GC with a TCD. Mass loss was determined as described above for the dairy manure reactor.

2.3. Data analysis

Measured biogas volume was standardized to 101.325 kPa and 0 °C using the "stdVol" function in the biogas package (v. 1.1.0) [5]. Details on the calculations are given in the Supplementary material. Methane production was calculated for each biogas removal event as the product of measured x_{CH_4} and standardized volume and cumulative production was calculated by summing these values. For the batch reactors, x_{CH_4} was estimated by linear interpolation for dates when composition was not determined using the "cumBg" function in the biogas package (v. 1.1.0) [5].

The gravimetric method was applied to each observation using two estimates of x_{CH4}: the "true" measured value (based on total CH_4 and CO_2 volumes determined using the volumetric method) and an "approximate" value, meant to represent an estimate that could be made with limited measurements or based on literature data. The approximate value of x_{CH4} was 0.60 for batch reactors with cellulose, and 0.70 for all others. No approximate value was used for three reactors that contained no inoculum. Values of 0.60 and 0.55 were used for semi-continuous manure and biomass reactors, respectively. Biogas pressure P_b was assumed to be 152 kPa for batch reactors, and the standard pressure (101.325 kPa) for other reactors. Results from batch reactors were corrected for N_2 originally present in the headspace as described in the supplementary material. Calculations were carried out using the "cumBg" and "mass2vol" functions in the biogas package (v. 1.1.0) [5].

Gravimetric and volumetric results were compared by linear regression using the "lm" function in R (v. 3.2.0) [6], based on final cumulative results for the batch reactors. The difference between the two methods was determined for each reactor (gravimetric minus volumetric). The standard deviation (s) of this difference provides an approximate estimate of the random error in the gravimetric method (approximate because it also includes error from the volumetric method). Relative difference was calculated by dividing differences by the mean value of the two results.

3. Results and discussion

For most batch reactors gravimetric results were close to volumetric results over a wide range in CH_4 volume (Table 1, Figs. 1 and 2). However, gravimetric results were slightly higher overall: linear regression of gravimetric versus volumetric results showed an intercept indistinguishable from zero (95% confidence limits: −10 and 105 cm^3) but a slope slightly greater than unity (95% confidence limits: 1.020 and 1.060 $cm^3\ cm^{-3}$). Based on final cumulative production, the relative difference was <10% for 85 of 111 reactors, and <20% for 104. With approximate values for x_{CH_4}, variability increased (Fig. 2) (95% confidence limits: −82 and 120 cm^3 and 1.05 and 1.12 $cm^3\ cm^{-3}$, while 61 and 96 reactors had relative difference <10% and <20%, respectively). Four observations of apparent mass