Korištenje izračuna biokemijskog potencijala proizvodnje metana (BMP) za projiciranje i poboljšanje performansi anaerobnih fermentora

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Sažetak
Pomoću metode izračunavanja bikoemijkog potencijala proizvodnje metana(BMP) možemo prikazati anaerobnu razgradivost pojedinih supstrata. Koristeći BMP metodu moguće je uz relativno niske troškove, te mogućnost ponavljanja, usporediti anaerobnu razgradivost i potencijal proizvodnje bioplina između različitih supstrata. BMP metoda može biti korištena kako bi se utvrdila količina organskog ugljika u određenom materijalu koji anaerobno može biti pretvoren u metan, a na osnovu čega se lako procjenjuje efikasnost proizvodnje bioplina određenog materijala, koji se koristi kao supstrat. Podatke koje dobijamo na osnovu BMP metode, koriste nam pri procjeni vrijednosti potencijalnog supstrata za proizvodnju bioplina, kao i pri optimalizaciji operativnog dizajna anaerobnog fermentora. Prikazane su procedure za izračunavanje proizvodnje bioplina i sadžaja metana putem BMP metode, koje se koriste u Laboratoriju za ispitivanje otpadnih materijala (Iowa State University), te na koji se način dobiveni rezultati mogu koristiti.

Ključne riječi: anaerobna fermentacija, biokemijski potencijal, metan, stočna gnojovka

Use of Biochemical Methane Potential (BMP) Assays for Predicting and Enhancing Anaerobic Digester Performance

Abstract
A Biochemical Methane Potential (BMP) assay provides a measure of the anaerobic digestibility of a given substrate. The use of BMPs provides a relatively inexpensive and repeatable method to make relative comparisons of the anaerobic digestibility and potential biogas production between various substrates. Biochemical Methane Potentials can be used to determine the amount of organic carbon in a given material that can be anaerobically converted to methane and to evaluate potential biogas production efficiency of the anaerobic process on a given material. The information provided by BMPs is valuable when evaluating potential anaerobic substrates and for optimizing the design and operation of an anaerobic digester. This paper describes the BMP assay procedure used in the Agricultural Waste Management Laboratory at Iowa State University for quantifying both biogas production and methane content and it describes how the results can be used.

Key Words: anaerobic digestion, biochemical methane potential, animal manure

Introduction

Controlled anaerobic digestion of animal manures is primarily used to reduce odors in waste management systems, to reduce the organic strength of a waste stream, and produce energy-rich biogas. Capturing and using the methane (CH_4) in biogas also reduces greenhouse gases and in some cases can be used to generate marketable carbon credits. These benefits have led to increased interest and use of anaerobic digesters at animal production and product processing facilities. Careful planning and accurate system design are necessary to optimize performance and maximize cost recovery.

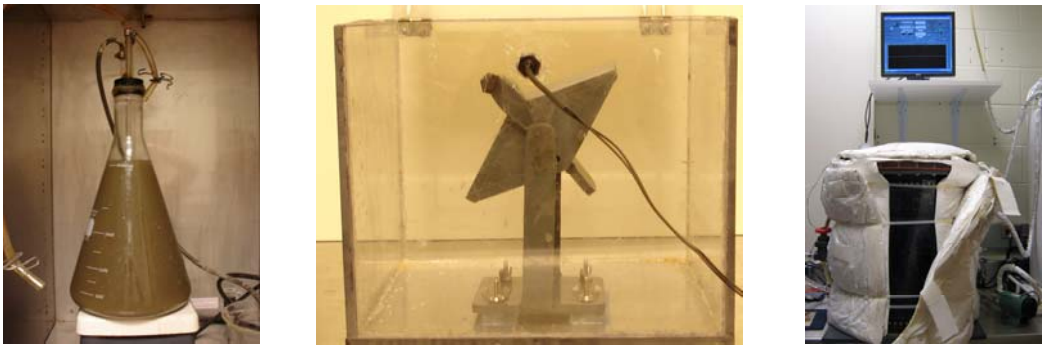
Multiple sources are available to provide estimated operational parameters of anaerobic digesters based on theoretical data and on data collected from reactors operating with agricultural waste streams (Balsam, 2006; Burke, 2001; USDA-NRCS, 2007). However, use of those estimates for actual design parameters can lead to under or over estimated digester system performance. Biochemical methane potential assays (BMPs) are an alternative available to assist with site specific design criteria. Through stoichiometric conversion, CH_4 production is directly related to organic degradation; 395 mL CH_4 equals 1 g COD reduction (Speece, 1996). Methane production can vary by reactor feedstock and due to multiple digester system factors. At animal production facilities, the following sources of methane production variability have been identified; animal ration, manure solids content, frequency of manure collection, anaerobic reactor temperature, reactor residence time, and manure pH. Biochemical methane potential assays are used to 1) determine the concentration of organics in a wastewater that can be anaerobically converted to CH_4, 2) to evaluate the potential efficiency of the anaerobic process with a specific wastewater, 3) to measure residual organic material amenable to further anaerobic treatment, and 4) to test for non-biodegradables remaining after treatment (Speece, 1996). The BMP test requires minimal labor and cost for set-up and monitoring as compared to larger feasibility studies, and it provides more accurate information for a specific wastewater than values obtained from literature. Literature related to BMP assays for agricultural wastes shows assays have been used to evaluate a variety of issues. Labatut and Scott (2008) used BMPs to determine which available food residues could be co-digested with manure from a dairy and at what ratio the residue should be mixed to improve the economic viability of the on-farm digester. Similarly, BMPs were used by Lovanh et al. (2008) to determine the effect amending swine manure with poultry litter had on methane production rates. Kirk and Bickert (2004) utilized BMPs to evaluate manure slurry from multiple points in a dairy manure treatment system to determine the optimal location of the digester within the treatment system for maximum gas production and pathogen reduction. To establish reactor inoculation conditions and feeding regimes for efficient start-up and operation of a full scale digester, Nohra et al. (2003) performed psychrophilic BMPs with swine slurry.

The BMP assay process was first established by Owen et al. (1979) as a simple and inexpensive procedure to monitor relative anaerobic biodegradability of substrates. The paper explains the BMP assay method used in the Agricultural Waste Management Laboratory at Iowa State University, and discusses how results can be interpreted and used.

Materials and Methods

The BMP assay involves incubating wastewater inoculated with anaerobic bacteria for a period of 30 to 60 days. Incubation temperature is usually 35ºC, but can be varied depending on the system being considered. Multiple wastewater to inoculum ratios are usually assayed. Biogas production is monitored throughout the test, and biogas is analyzed for CH_4 content. A control containing only inoculum and water is used to determine CH_4 production resulting from the inoculum alone. Basic requirements for a BMP include anaerobic inoculum, ability to analyze COD and volatile solids, assay bottles (250 mL) with septums, compressed CO_2 and N gas, an incubator (or other form of temperature control), an orbital shaker, a gas syringe, and a method for analyzing CH_4 in the biogas.

Inoculum for the assays is generally acquired from an active anaerobic reactor. The inoculum used at the Agricultural Waste Management Laboratory at Iowa State University was started in a 4-L flask placed on a stir plate in an incubator at 35ºC (Figure 1a). Biogas production in the inoculum flask reactor was monitored with a tipping bucket gas meter (Figure 1b) and substrate was injected on a daily basis. Consistent gas production from the inoculum reactor is an indicator of good bacterial health, and consistent gas production should be achieved before using the inoculum in BMP assays. To meet the demand for BMP assays in the laboratory, a new inoculum reactor was built (Figure 1c). The size was increased from 4 to 60 L, and the process controls were automated. Directions for making the substrate to feed the inoculum are shown in Table 1.



(a) (b) (c)

Figure 1. Maintaining an inoculum source for biochemical methane production assays; (a) initial 4-L reactor, (b) tipping bucket gas meter, (c) automated 60-L inoculum reactor.

Table 1. Directions for making 1 L of substrate to feed to the inoculum. The mixture should be supplied to the reactor at a rate of 50 mL / L reactor volume / day.

Substrate contents: high protein-dry dog food, trace nutrient, and sodium bicarbonate
Directions: Mix 22.5 g dry dog food with 0.5 L de-ionized water, soak overnight. Add 3.3 g sodium bicarbonate and 1 mL of trace nutrients. Blend mixture and bring volume to 1 L using de-ionized water. Keep refrigerated.
Trace Nutrients – Mix the following with 1 L of de-ionized water • Ferrous Chloride, $FeCl_2.4H_2O$ 10 g • Cobalt Chloride, $CoCl_2.6H_2O$ 2 g • EDTA 1 g • Manganous Chloride, $MnCl_2.4H_2O$ 0.5 g • Resazurin 0.2 g • Nickelous Chloride, $Ni_2Cl_2.6H_2O$ 0.142 g • Sodium Selenite Anhydrous, Na_2SeO_3 0.123 g • Aluminum Chloride, $AlCl_3.6H_2O$ 0.09 g • Boric acid, H_3BO_3 0.05 g • Zinc Chloride, $ZnCl_2$ 0.05 g • Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ 0.05 g • Calcium Chloride, $CaCl_2.2H_2O$ 0.038 g • Hydrochloric acid, HCl (37.7%) 1 ml

Setting up the Assay The first step is to determine the COD and VS of the inoculum and of the wastewater to be assayed. The VS concentration of the inoculum will vary with time and should be measured before starting each assay. Using the VS concentration, the quantity of waste and inoculum to be added to the assay bottle are determined. The goal is to obtain a measureable, but not excessive rate of CH_4 production for monitoring during the assay. The substrate to inoculum ratios selected for a BMP assay bottle can vary, but they are generally around 1 g COD/ g VS. Substrate to inoculum ratios may also be shown on a VS basis. Because endogenous CH_4 production (self-digestion of the inoculum) is accounted for with the control and then subtracted from the total methane production in the assay bottle, the substrate to inoculum ratio should not affect the final volume of methane produced. The substrate to inoculum ratio should control the rate at which methane is produced. For a 250 mL assay bottle, the volume of liquid should be 150 mL. This volume

can be reached by adding de-ionized water to the bottle once the required mass of inoculum and substrate are added.

The control contains the quantity of inoculum added to the other assays plus de-ionized water to bring the volume to 150 mL. Each assay should be performed in triplicate. To insure CH_4 production is not limited by substrate or inoculum availability multiple substrate to inoculum ratios should be tested. After correction for endogenous methane production, results are normalized to volume of gas per mass of assayed COD. Normalized results between ratios are compared to insure the assay was not substrate limited.

After filling, the head space above the liquid in the assey bottels is purged with 30% CO_2 and 70% N gas to enhance the anaerobic condition in the bottle. The gas mixture should enter the bottle at 1 L/min for 5 minutes, then seal the bottle with a rubber septum and placed on a shaker (150-200 rpms) in a temperature controlled location (usually 35°C). Measure the biogas by inserting a needle into the septum. Allow the gas pressure in the bottle to displace the syringe plunger and record the displaced volume. These steps are shown in Figure 2. Biogas removed from the assay bottles should be analyzed for CH_4.

(a) (b) (c) (d)

Figure 2. Steps for setting up and maintaining BMP assays; (a) after adding liquid, purge bottle with CO_2/N gas mixture, (b) seal bottle with rubber septum, (c) place bottles on shaker in incubator, (d) insert gas syringe needle to measure gas via volume displacement.

Assay Results Biogas volume can be shown as cumulative biogas production. Total biogas should be corrected to account for the endogenous biogas resulting from the inoculum by subtracting the control biogas production from the total of each assay. A graphical representation of cumulative biogas production is shown in Figure 4. Use the CH_4 content to convert total biogas produced to total methane produced. Total methane production and total biogas production can then be normalized to volume of gas per mass of assayed COD. See example in Figure 3. To determine the percentage of digestible substrate COD, use the stoichiometric conversion of 0.395 mL CH_4 per 1 mg of COD reduction (see Figure 3).

Discussion

The normalized results provided (volume of CH_4 per mass of COD assayed and volume of biogas per mass of COD assayed) provide very useful informaiton. Used with an estimate of the mass of COD to be anaerobically digested in a reactor for a given time period, these values can be used to assist in determining the biogas storage volume for the reactor, size the energy use component (i.e. engine or boiler size), evaluate potential carbon credits, and calculate a rate of return on the investment. Additionally, if you are considering co-digestion of multiple wastewaters a BMP assay is useful to determine which alternatives provide the greatest benefits. The percentage of anaerobically digestible COD also provides a good estimate of the digester efficiency that could be achieved.

Example Calculations: Mass COD in assay = 280 mg,
Biogas Volume = 125 mL, % CH_4 in Biogas = 65%

Volume CH_4 = Biogas volume (% CH_4 in Biogas)
Volume CH_4 = 125 mL (65%) = 81.3 mL CH_4

$$\frac{\text{Volume } CH_4}{\text{Mass COD}} = \frac{81.3 \text{ mL } CH_4}{280 \text{ mg COD}} = \frac{0.29 \text{ mL } CH_4}{\text{mg COD}}$$

$$\frac{\text{Volume biogas}}{\text{Mass COD}} = \frac{125 \text{ mL biogas}}{280 \text{ mg COD}} = \frac{0.45 \text{ mL biogas}}{\text{mg COD}}$$

$$\text{Digestible COD (\%)} = \frac{\text{Volume } CH_4}{\text{Mass COD}} \times \frac{1 \text{ mg COD}}{0.395 \text{ mL } CH_4} \times 100$$

$$= \frac{81.3 \text{ mL } CH_4}{280 \text{ mg COD}} \times \frac{1 \text{ mg COD}}{0.395 \text{ mL } CH_4} \times 100 = 73.5\%$$

Figure 3. Equations showing normalized gas production and anaerobically degradable COD.

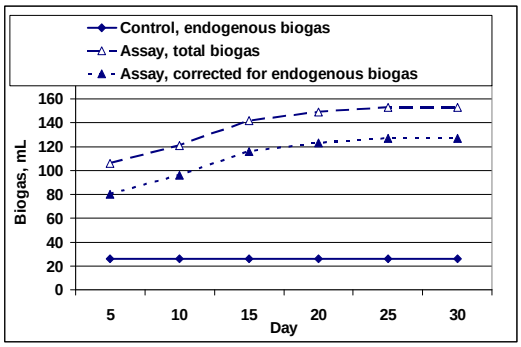


Figure 4. Cumulative biogas production shown with total and corrected volumes.

Conclusions

Anaerobic digestion benefits have led to increased interest and use of the technology. However, capitol costs of anaerobic digestion systems are high and careful planning and accurate system design are necessary to optimize performance and maximize return. Biochemical methane potential assays (BMPs) provide a realistic estimate of the anaerobic digestibility of a given substrate. The BMP assay can be used to generate data from the actual wastewater considered for anaerobic digestion that should be more accurate than book and literature values that are available to assist with site specific design criteria. Additionally BMP assays are relatively inexpensive and require minimal labor as compared to larger feasibility studies.

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