Name: Date: Class/Hour:

ANAEROBIC DIGESTION

INTRODUCTION

An anaerobic digester is a biogas recovery system. During anaerobic digestion, bacteria break down manure in an oxygen-free environment. One of the natural products of anaerobic digestion is biogas, which contains between 60 to 70 percent methane, 30 to 40 percent carbon dioxide, and trace amounts of other gases. This is different than composting because composting uses aerobic bacteria that need oxygen. The biogas released is then only carbon dioxide.

The key to any anaerobic digester is the substrate, which is the feedstock of the digester. Generally speaking, the feedstock can be comprised of anything that can be converted into methane by anaerobic bacteria. Cities have been using anaerobic digesters to deal with wastewater since 1895, when England developed an anaerobic digester that used wastewater to power streetlamps. It was not until the 1970s when farms in the U.S. experimented with digesters. Farm digesters have seen a lot of growth since 2000, and a number of cities are converting their aerobic treatment systems into anaerobic digesters.

One component of most substrates can be manure. However, co-substrates can be added to increase production of methane. There is a balance to this addition, though. Too much high strength substrate can cause an imbalance in the bacteria population equilibrium. In a digester system there are at least three different active bacteria populations: acetogens, hydrogenic bacteria, and methanobacteria.

Acetogens produce acetate, through acetogenesis, from a variety of energy and carbon sources. They are anaerobic bacteria. Hydrogenic bacteria are characterized by the consumption of organic acids and production of molecular hydrogen. Methanobacteria reduce carbon dioxide and produce methane as a waste product.

The acid forming bacteria are the first to start breaking down the substrates into smaller organic molecules which are typically carboxylic acids. If too much acid is formed, the pH drops below the optimal range for the other bacteria and they become dormant. If they become dormant, there will be no methane formed.

In this experiment, you will prepare a range of concentration of substrate to seed stock and determine the optimal concentration for methane production. These samples will be maintained at a constant temperature for one to two weeks.

Each week, you will determine the total amount of gas produced and the percentage of carbon dioxide by titration. The methane concentration will then be determined by the difference.

PROCEDURE

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PART 1: SETUP

1. Weigh out about 30-35g of a seed solution obtained from a nearby anaerobic digester. This is either from a wastewater treatment plant or a farm digester.

2. Place in the bottle that will be sealed for seven days.

3. Add varying amounts of the substrate (waste stream) that will be tested. Typically, this is about 1.0%, 1.5%, 2.0%, or 3.0% by mass of seed solution.

4. Flush nitrogen through the bottle for 2 minutes at a steady, gentle flow.

5. Seal the container and place in a constant temperature apparatus at 35°C or 38°C until the next week.

6. Determine the pH, total solids, volatile solids, and COD (chemical oxygen demand) of the seed solution and substrate if time allows. (Some of this information may be provided by the instructor.)

PART 2: TOTAL GAS DETERMINATIONS

After 1 week, determine the amount of biogas produced over the last week.

Note: Extra caution is required, depending on what type of container the biogas is produced in. If it is produced in a solid container, the valve needs to be closed after the syringe is filled to only about 40% capacity. Otherwise, the syringe plunger will expand beyond the end of the syringe to reach room pressure. A 60mL syringe is used, along with a needle and needle valve in the closed position, when inserted into the sealed bottle.

1. Keep a hand on the plunger with pressure to keep it from blowing out the end. The syringe is only allowed to fill up partway so that the pressure is equilibrated to room pressure before it is removed. The syringe is equilibrated to room pressure after closing the valve by pulling the plunger further out and letting it pull back in slightly.

2. After the syringe pressure is equilibrated, remove it from the valve. This decreases the amount of gas leakage from the bottle.

PROCEDURE (cont.)

3. Inject this sample into the carbon dioxide trap prepared in the next steps. Only 50-60mL total of the biogas is injected into the carbon dioxide trap.

4. Continuously remove gas until there is no more. Follow the pressure equilibrating step each time.

BIOGAS RATIO BACKGROUND

Biogas quality is typically determined by the percent methane and amount of hydrogen sulfide that needs to be removed. The biogas sample is too small to determine the hydrogen sulfide content without the use of a gas chromatograph (GC). Typically, the methane content is determined by using a GC and a different column and detector than that used for hydrogen sulfide. If such a GC is available and is used the following titration step is bypassed. The remainder of the gas not determined to be methane in the GC is deduced to be carbon dioxide.

The following titration is used to determine the amount of carbon dioxide. The amount of methane is determined from the difference. In this experiment, a two-step titration is performed on a gas trap solution. The first step in the titration is to neutralize the strong base. The second step is the titration of HCO_3- to H_2CO_3. This titration determines how much CO_2 from the gas sample is trapped by the sodium hydroxide.

Trap

$NaOH + CO_2 \rightarrow Na+ + HCO_3-$

Neutralization that happens above pH of 8

$NaOH + HCl \rightarrow NaCl + H_2O$

Neutralization that happens around pH of 5

$HCO_3- + HCl \rightarrow H_2CO_3 + Cl-$

NOTES

PROCEDURE (cont.)

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PART 3: TITRATING SAMPLES

PREPARING THE CO_2 TRAP

1. Pipette 5mL of 0.50M NaOH into a 60mL sample vial and close with a rubber stopper and aluminum cap using the crimper.

2. Take a 50 to 60mL gas sample from the test vial and inject into the sealed vial. Record the volume injected.

3. Swirl the solution for 2-4 minutes to ensure that all of the carbon dioxide reacts with the hydroxide solution.

DETERMINATION OF CO_2 BY TITRATION

1. Remove the aluminum cap and rubber stopper.

2. Add 2 to 3 drops of Phenolphthalein to the solution.

3. Titrate the solution with 0.10M HCl. (Note: pink color in solution may initially disappear after the first 5mL of titration, well before the equivalence point is reached. If this happens, add 2 more drops of indicator to solution and continue titration.)

4. Once the end point is reached, record the volume on the burette.

5. Add 2 to 3 drops of Methyl Orange indicator to the solution.

6. Continue titration with 0.10M HCl to the second end point.

Note: The same titration should be performed using a blank sample of 0.50M NaOH solution to determine if there is any carbon dioxide dissolved in the stock solution. This titration is performed on all samples prepared in the previous week.

PROCEDURE (cont.)

To determine the % of the gas sample that is carbon dioxide, determine the moles of carbon dioxide from the titration.

mL HCl (for second end point) x ~0.10M HCl
-> moles HCl = moles CO_2

The formula 22.4L = 1 mole of a gas at standard conditions is used to determine the mL of gaseous CO_2.

To be more precise, the temperature and pressure of the room is used along with PV = nRT.

The remaining volume of the biogas contains a very small amount of water vapor and other gases, such as hydrogen sulfide. For this laboratory, these other small volumes are ignored, and the remainder of the gas is assumed to be methane and the original nitrogen gas.

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