BIOGAS POTENTIAL OF HOUSEHOLD WASTE FOR USE IN HIGH SCHOOL SCIENCE CURRICULUM

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ABSTRACT

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Many high school science curriculums discuss the energy crisis and the role of scientists using renewable technologies to find solutions. Discussing anaerobic digestion in high school science curriculum introduces the concept of renewable energy and offers a "hands on" experience producing biogas. The purpose of this paper is to demonstrate methodology in evaluating household waste products for biogas production for inclusion in high school science experiments. Samples were compiled with different combination of fruit (banana's) vegetable (spinach) and raw manure. Bioreactors were tested for COD using a HACH kit and alkalinity through titration. Buffering agents and trace metals were added to increase the alkalinity of the sample and provide micronutrient for microbial population growth.

COD test results indicate issues with sample preparation and analysis. Error could be due to large particles clogging the pipet during sample preparation, errors associated with the dilution procedure, sample interference with the COD test procedure, or inaccuracies with the COD HACH kit. Biogas production from the 100F and 100M were greater than any of the mixed samples. Average biogas production was increased with the amount of manure that was used to seed the sample. Fruit samples showed the highest gas productivity. However, the gas production is most likely a combination of ethanol and ethyl acetate during the first few days followed by biogas production similar to other samples analyzed. Biogas production of 100F samples significantly reduced after day three, falling below 100M, 20V 80M and 20F 80M. This data suggests that samples with higher manure content continually produce biogas where other samples appreciably reduced biogas production around day 15.

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INTRODUCTION

Anaerobic digestion of waste to produce biogas is a fascinating field of study that has gained momentum with the exploration of renewable energy sources. Many high school science curriculums discuss the energy crisis and the role of scientists using renewable technologies to find solutions. Anaerobic digestion is proven technology as a sustainable energy source to produce biogas. It offers addition significance to the renewable energy debate by being an effective means of revolving a waste product into energy. Discussing anaerobic digestion in high school science curriculum introduces the concept of renewable energy sources to young minds early in their scholarly career and challenges individual thought processes.

Anaerobic digestion is the process of stabilizing or breaking down a waste product by microorganisms in the absence of oxygen. It can be greatly simplified by stating as a two step process where microorganisms break down and use the energy in the waste product to grow and sustain their populations. Two basic groups of microorganisms are used in the anaerobic digestion process. Fermentative bacteria take the waste source and create long chain fatty acids, a process called fermentation. Aceticlastic methanogens take the fermented products and produce carbon dioxide and methane. The fermentation process will produce acid products (acetate, butyrate, and propionate) which will reduce the pH of the waste product if it is not buffered. Fermentative bacteria do not perform well at pH less than 4, while methanogen bacteria do not perform well at pH greater than 6. Therefore, waste media used in anaerobic digestion must have adequate buffering capacity to maintain the pH between 4 and 6 or a buffer should be added.

There is limited energy available for microbial growth through the anaerobic digestion process, therefore, anaerobic bacteria populations grow slowly and take a long time to build their population. This process can take up to two years in anaerobic lagoons used to treat animal waste in cold climates. For this reason, a seed source of bacteria is typically used to establish a reasonable amount of anaerobic bacteria to speed up the anaerobic digestion process when starting anaerobic

digesters. In addition, lack of trace metals in the waste product will also inhibit bacterial growth. Therefore trace metal concentrations must be adequate to sustain bacteria populations.

There are many experiments developed to explore anaerobic digestion in high school curriculums. One such experiment suggests that students place waste media into a 2 liter plastic bottle with a balloon on the top to capture biogas production. It is the students who determine which waste product should be added to their individual digester. It is not surprising when biogas production was not experienced in any of the digesters due to lack of a bacterial seed source and conditioning of the waste with trace metals and pH buffering. The purpose of this paper is to demonstrate methodology in evaluating household waste products for biogas production for inclusion into high school science experiments. Following this methodology will aid students in achieving biogas production and facilitate interest in anaerobic digestion. Students will understand that the technology is achievable and can be effective as a renewable energy source.

MATERIAL AND METHODS

Sample Composition

Samples were compiled with different combination of fruit (banana's) vegetable (spinach) and raw manure (collected from the MSU dairy heifer barn feed lane). Measured components (by weight) were placed into a blender (typical household blender - Oster 10 speed osterizer blender) with 100 mL of deionized water (DI water) and ground into a pulp like consistency. Samples were then placed in a 0.5 L glass bottle and weighed for the initial weight. DI water was added to each sample to increase the volume to 400 mL and weighed again for the final weight. The 100V sample was modified to 50 percent due to limited spinach availability. Therefore, for the 100V sample, 100 grams of spinach was placed in a blender with 100 mL of water prior to blending. DI water was then added to increase the volume to 200 mL. Sample compositions are shown in Table 1.

Table 1. Sample Composition

	Vegetable	Fruit	Manure	Initial Weight	Final Weight	Final Volume
	grams	*grams*	*Grams*	*Grams*	*Grams*	*mL*
80V 20M	160.0		40.0	273.0	367.7	400.0
80F 20M		160.0	40.0	289.4	361.1	400.0
40V 40F	80.0	80.0	40.0	235.0	377.0	400.0
20V 80M	40.0		160.0	243.0	349.0	400.0
20F 80M		40.0	160.0	290.0	391.0	400.0
200 M			200.7	263.3	360.5	400.0
200 F		200.8		292.1	374.1	400.0
200 V	100.5			192.8	232.1	400.0
5M 95F		190.3	10.5	285.7	361.3	400.0
10M 90F		179.5	20.1	286.0	358.8	400.0
15M 85F		170.6	30.5	283.7	357.3	400.0
V = Vegetable **F = Fruit** **M = Manure**						

Fruit and vegetable were dried in an oven at 105ºC for 72 hours to determine the dry weight. Dry weight for the manure samples was taken from the ASABE Standard D384.2.

Bioreactors were created by adding 50 mL of sample to a 160 mL BOD bottle. Each sample was replicated three times. One mL of sample was removed from each of the BOD bottles and diluted with 99 mL of deionized (DI) water. The diluted sample was analyzed for chemical oxygen demand (COD) in triplicate and is discussed later. Trace metals were added to the 49 mL of sample in the BOD bottle in the amount of 0.25 mL and 0.42 grams of $NaCO_3$ (increase buffering capacity) were added to each sample. Nitrogen gas (N_2) was blown into sample bottles prior to sealing to remove oxygen from the headspace. Sample BOD bottles were sealed with plastic septa and aluminum caps. Samples were then placed in a New Brunswick Scientific Excella E24 Incubator Shaker at 37ºC and 100 rpm.

COD measurement

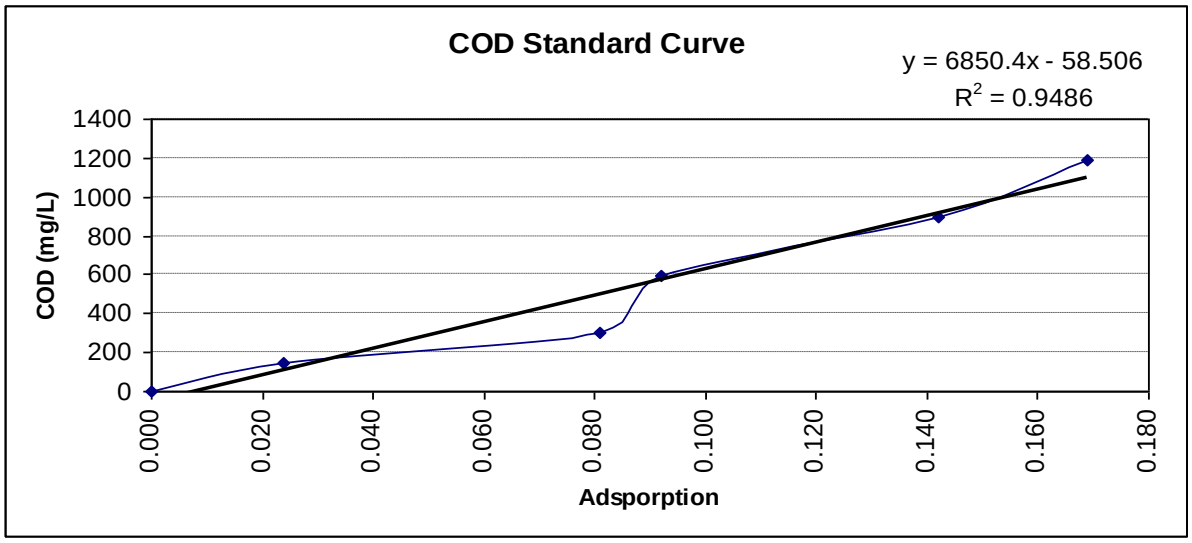
COD analysis was conducted using Hach digestion solution for COD and reading adsorption from the samples with a Spectronic 21 D by Milton Roy. A COD standard was prepared by diluting 0.1267 g potassium hypoclorite (KHP) in 100 mL of DI water to create 1490 mg/L COD. The COD standard was then diluted with DI water to create a standard curve with COD values from 150 ppm to 1500 ppm. Standard dilution volumes are shown in Table 2.

Table 2. Standard Curve Values

Dilution	Stock	DI Water
	mL	mL
Blank	0	10
149	1	9
298	1	4
596	2	3
894	3	2
1192	4	1
1490	10	0

COD absorbance values were graphed vs. the calculated COD value in excel using a scatter plot. A linear regression analysis was conducted to determine the relationship between absorbance and COD values. The standard curve used in COD calculations in shown in Figure 1.

Figure 1. Standard Curve



There is no statistical difference between the 1192 and 1490 ppm standard, therefore, the standard curve was determined from zero to 1192 ppm. The 298 mg/L COD sample shows a significant deviation from the regression equation. Most likely this is due to absorbance evaluation of the standard curve two weeks after samples were digested. All other samples correlate well with the linear regression.

Diluted samples (discussed in sample preparation) were mixed by filling a two mL pipette and discharging back into the diluted mixture three times before removing 2 mL of sample and placing into a Hach COD vial. COD vials were prepared with a strong acid solution by the manufacturer. Samples were shaken and then placed in a Hach COD reactor at 150 ºC for 120 minutes. Samples were heated in the reactor within 24 hours of adding the acid reagent. Sample adsorption was read within 7 days of heating. The Spectronic 21 D was powered a minimum of 30 minutes before sample analysis. A system blank was read every 25 samples to minimize instrument drift. The standard curve was evaluated at the beginning and end of reading samples.

Alkalinity Measurement

Diluted samples from the 80V 20M, 80F 20M, 40V 40F 20M, 20V 80M, and 20F 80M samples were analyzed for alkalinity following Standard Method 2320. 50 mL of diluted sample was titrated with 0.1 N H_2SO_4. Sample alkalinity ranged from 3,333 to 14,286 mg/L as CaCO3. Alkalinity was adjusted in each BOD vial with the addition of 5,000 mg/L as CaCO3 by adding 0.42 g $NaCO_3$ to each 49 mL sample.

Biogas Calculation

Theoretical biogas production was determined by assuming 80 percent of the sample COD is bioavailable and 0.35 m^3 of methane is produced for each kg COD. Methane composition of the biogas was estimated at 70 percent and carbon dioxide at 30 percent (ENE 804). Theoretical biogas production was estimated to be between 470 and 1,470 cm^3 over 30 days.

Biogas Measurement

Samples were prepared on January 31, 2011 and placed in an incubator at 37 ºC with 100 rpm rotation. All samples were vented on February 4, 2011 because gas pressure in 100F A, B and C was greater than pressure monitoring equipment (manometer) at that time. Monitoring conducted on February 7, 2011 was completed using two different gauges. A precision glide needle (B-D 25G $1^1/_2$) was attached to tygon R-3603 tubing and then connected to the pressure gauge. Connections were pressurized under water to evaluate for air leaks. The needle was inserted into the sample bottle septa to read the internal pressure of the sample. After each reading, a second needle was used to vent the sample to atmospheric conditions by releasing the existing pressure in the sample bottles. Gauge One is a Wika 316 SS Tube capable of 0-15 psi and was used to monitor 80V 20M, 80F 20M, 40V 40F 20M, 20V 80M, and 20F 80M samples because the maximum pressure was below 15 psi. All other samples were monitored with Gauge Two, Ashcroft Duralife 238A460-02 capable of 0 to 20 psi. All monitoring conducted after February 8th was conducted with Gauge One.

Volume of gas produced was calculated from the pressure (in psi) measurement assuming that standard condition of 22.4 mol air/L. Sample bottle capacity is equal to 160 mL. After 49 mL of

sample was added, there is 111 mL of headspace. Using the ideal gas law PV=nRT and assuming that $V_{initial}$ (Vi)= $V_{measured}$ (V_m), then $P_i/n_i = P_m/n_m$.

The assumption is made that the initial pressure in the bottle was equal to outside pressure, which is 14.5psi. Then, P_i =14.5psi. The reading from gauge is expressed in relative pressure, so the absolute value for the P_m is (14.5 + Reading) psi. The initial mole of gas in the bottle can be calculated by n_i= 111mL/(22.4mol air/L), and we got $n_m=P_m n_i/P_i$ = [(14.5 + Reading) *(111/22.4)]/14.5. And after converting n_m to volume under STP, the following equation was obtained to determine the volume of gas from the pressure reading in cm^3.

$$\frac{(14.5+\mathrm{Re}ading)*111}{14.5}-111=volumeofgas(cm^3) \qquad \text{Eq (1)}$$

RESULTS

COD Results

Sample COD was collected and measured during sample preparation as discussed above in Materials and Methods. Nine samples were analyzed for each sample group (three samples each taken from triplicate samples). Samples were analyzed assuming a 95% confidence interval, shown in Table 3. This analysis indicates that there were issues with COD sample preparation and /or analysis. Error could be due to large particles clogging the pipette during sample preparation, errors associated with the dilution procedure, or sample interference with the COD test procedure.

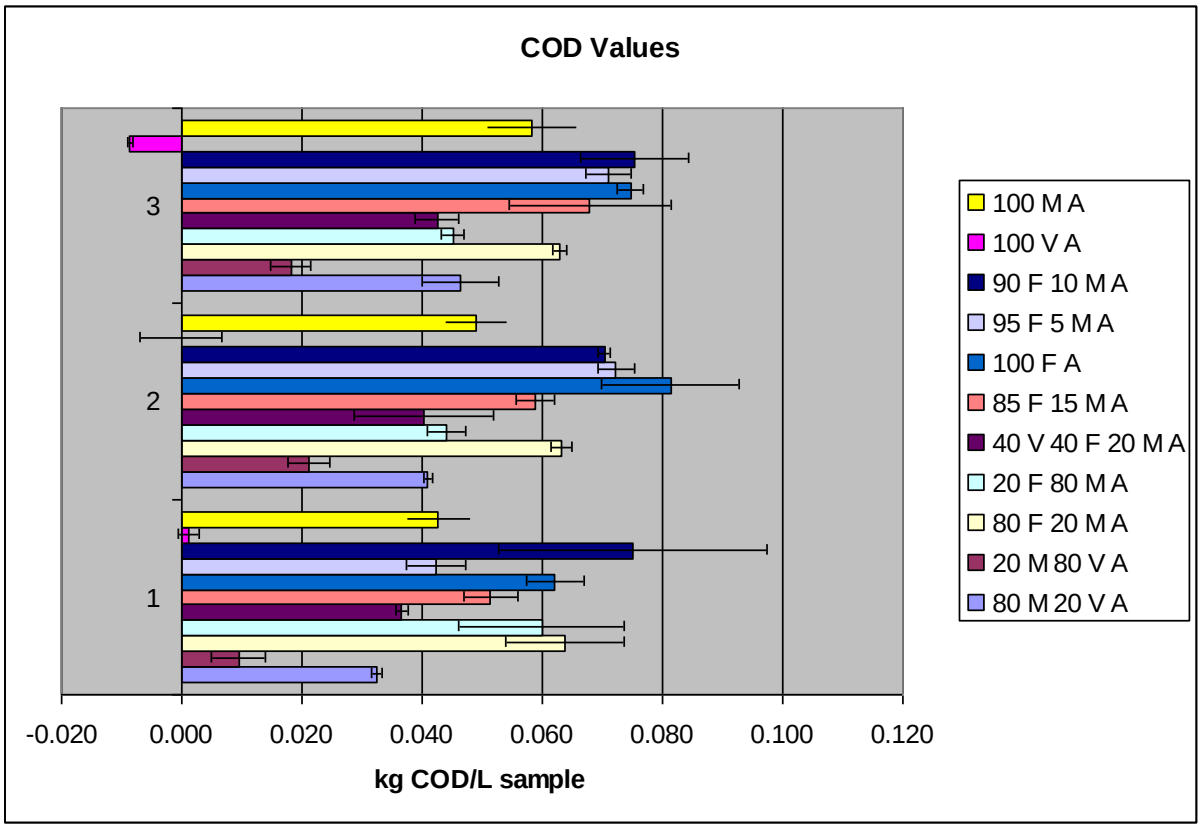
Table 3. COD 95% Confidence Interval

	0-5%	5%-10%	10%-15%	>15%
20 V 80 M			X	
80 V 20 M				X
80 F 20 M	X			
20 F 80 M			X	
40 V 40 F 20 M		X		
85 F 15 M		X		
100 F		X		
95 F 5 M				X

90 F 10 M	X			
100 V				X
100 M		X		

The statistical analysis indicates that the COD results are less accurate than desired. Sample triplicates were averaged and compared. 100F sample showed the highest COD value with an average of 0.073 kg COD/L and a standard deviation of 0.0098 kg COD/L. 100M sample average COD content is 0.05 kg COD/L with a standard deviation of 0.0079 kg COD/L. 100V samples showed nearly zero COD. This result indicates that the color of the spinach may have inhibited the COD evaluation. This could also explain why the 80V 20M confidence interval is greater than 15%. COD sample data is shown in Figure 2. Sample 1, 2 and 3 correlate with each triplicate sample.

Figure 2. COD Values in kg/L sample

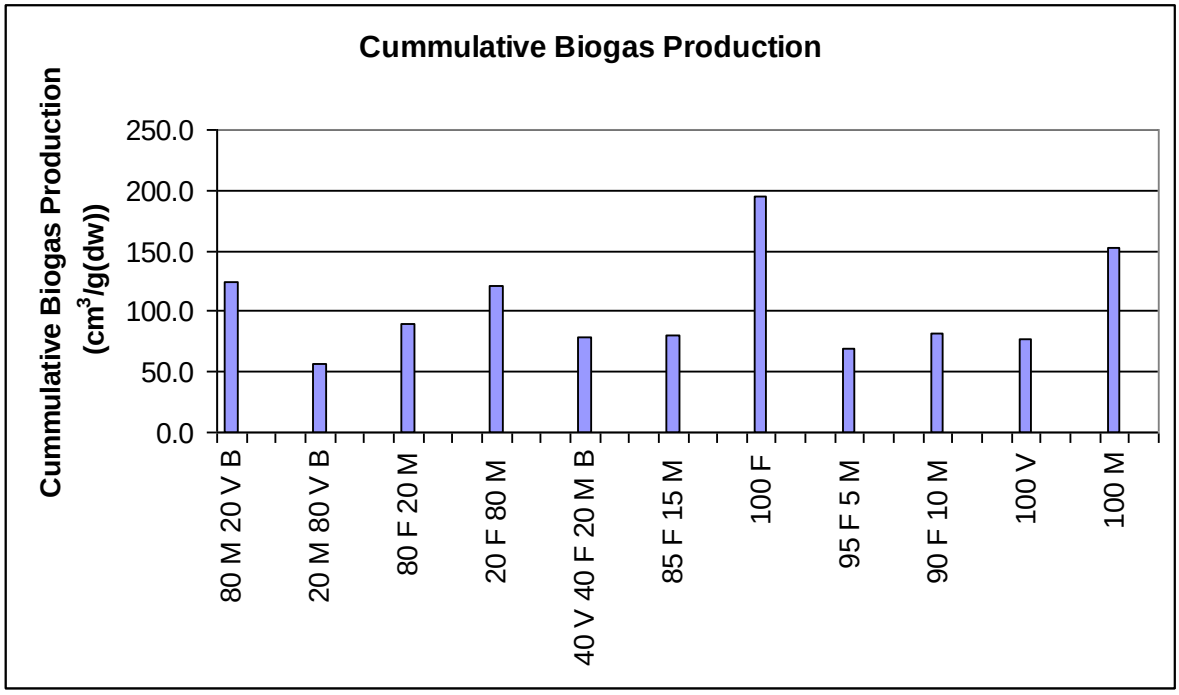


The error bars show the standard deviation for each triplicate sample.

Biogas Production

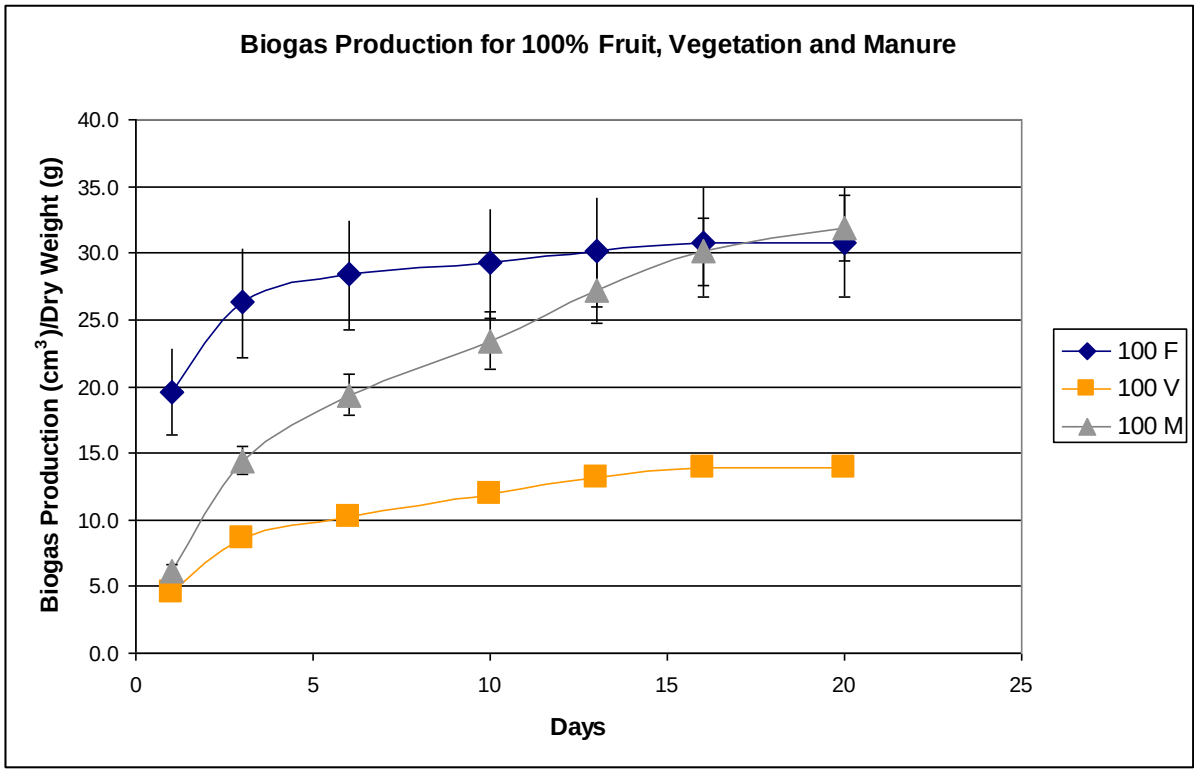
Biogas production was measured over 20 days. During that time the majority of the samples exhibited similar biogas production with the exception of the 40F 40V 20M samples. 40F 40V 20M samples showed relatively large variation among the three samples with a standard deviation of 4.9 $cm^3/g(dw)$. This sample group was the only group with a standard deviation value greater than 4 $cm^3/g(dw)$. Cummulative biogas production was highest for 100F and 100M samples, shown in Figure 3.

Figure 3. Cummulative Biogas Production



Daily biogas accumulation for 100M, 100F and 100V is shown in Figure 4. 100F exhibited the highest variability with the highest initial gas production. The average total amount of gas produced from 100F samples is 195.3 cm^3/g(dw). During the Feb 4th sampling event, the 100F group was the only group with a notable bulge in the septa indicating more gas production than other samples. The second highest gas production was from the 100M samples which produced an average of 152.6 cm^3/g(dw), 78% of the 100F samples.

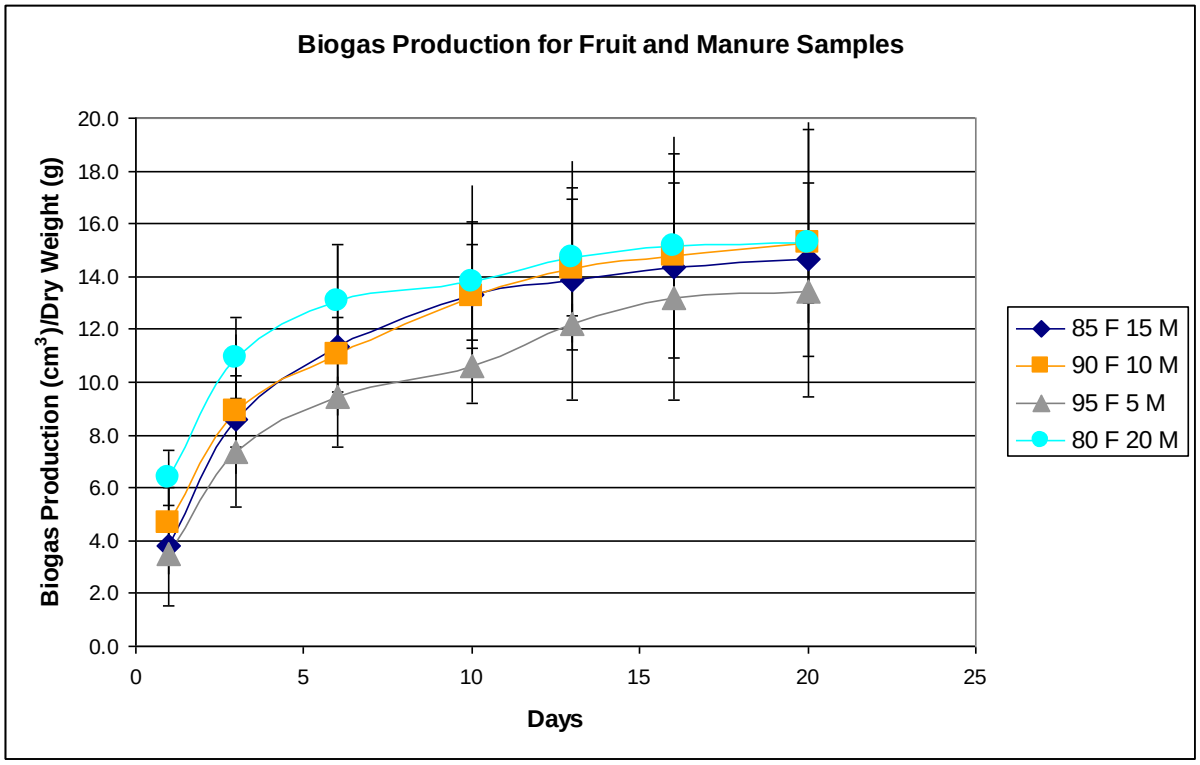
Figure 4. Biogas Production for 100% Fruit, Vegetable and Manure



Fruit biogas production was assumed to be due to the banana itself releasing significant amounts of ethanol and ethyl acetate due to ripening [1]. In those samples with banana and manure, the ripening process may be inhibited or microbial populations in the manure may be able to utilize the ethanol and ethyl acetate created by the banana. However, no publications related to this point were found. It is assumed that gas production due to ripening from the banana occurred during the start of the experiment while the banana was fresh. Biogas production appears to level off for the 100V and 100F samples by day 15 while the 100M sample continues to produce biogas.

Biogas production can be increased by providing a seed source to establish the microbial populations needed. Samples 95F 5M, 90F 10M, 85F 15M, and 80F 20M were evaluated to determine the influence of different seeding amounts using raw manure. The results are shown in Figure 5.

Figure 5. Biogas Production based on Manure Seed Rate

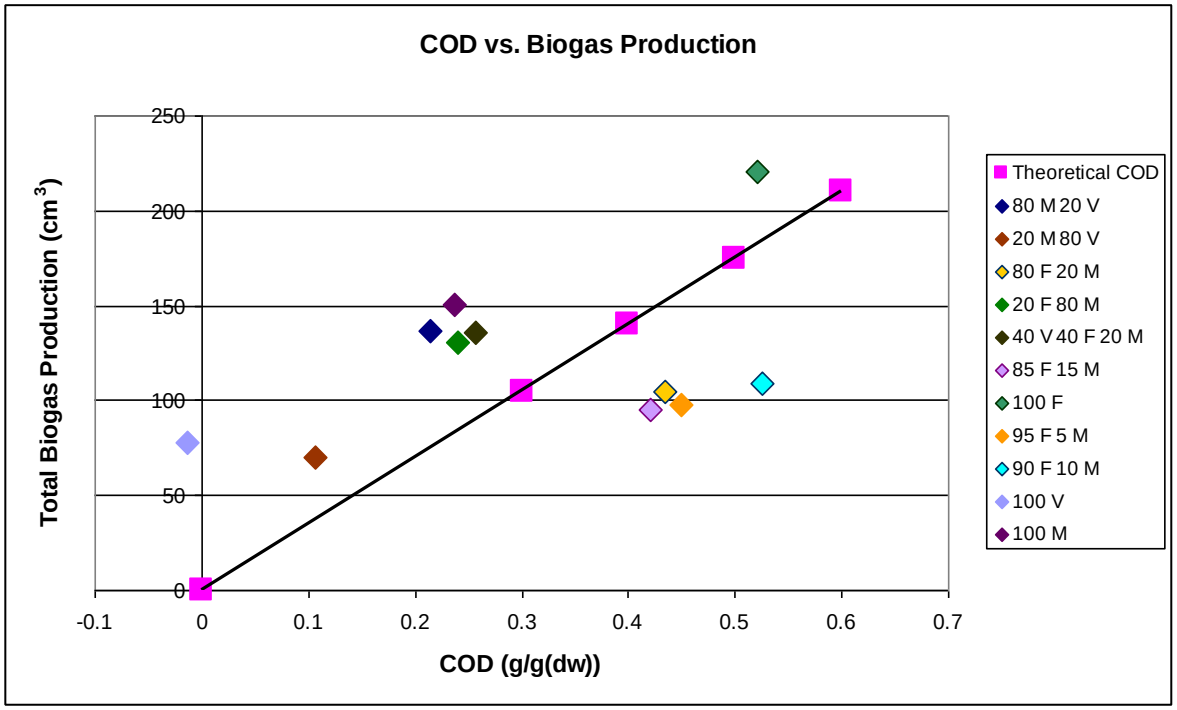


Average biogas production was increased with the amount of manure that was used to seed the sample. However, the increase in biogas production represents 19.6 cm^3/g(dw) which is 20 percent of the total biogas production for the 80F 20M sample. Due to the variability of each sample, the difference in manure seeding rates is not significant.

DISCUSSION

Biogas production was analyzed against the COD value in each sample, shown in Figure 6. The theoretical biogas production assumed during the material and methods was also graphed against this data. Theoretical biogas production overestimated total biogas production for the manure seed samples consisting mostly of fruit with varying levels of manure (5 to 20 percent).

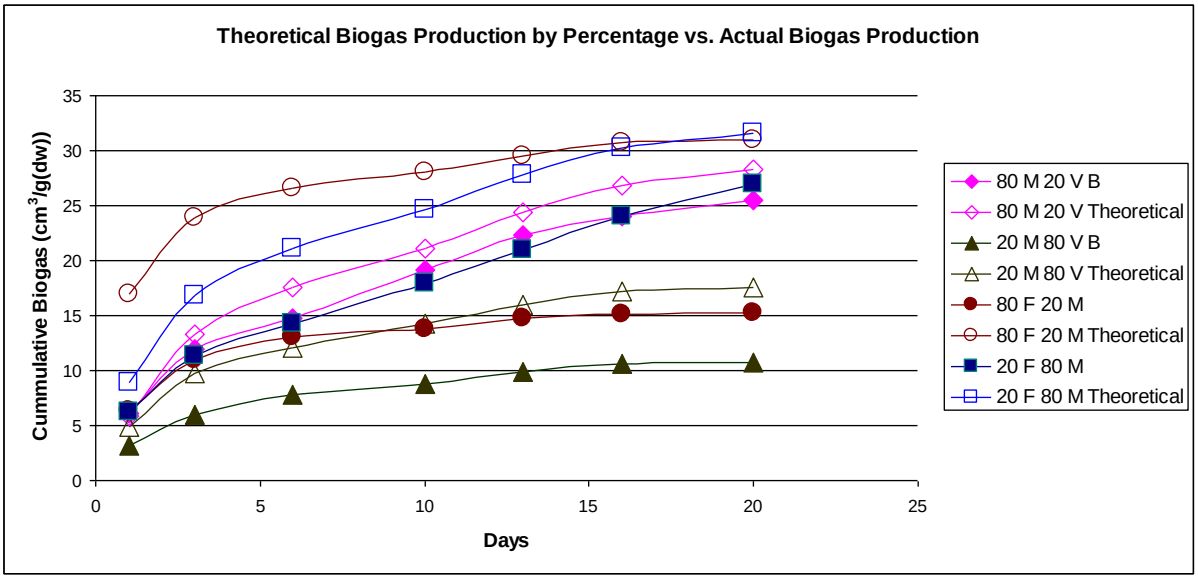
Figure 6. COD vs. Biogas Production



Of particular interest is the clustering of samples with higher percentages of manure (100M, 80 M 20 V, 20F 80 M) with the exception of 40 V 40 F 20M. This data suggests that samples with higher concentrations of manure will produce similar biogas quantities. Additional testing will need to be conducted to determine the optimum amount of manure for biogas production.

Theoretical biogas production by percentage was calculated using the 100V, 100F and 100M samples and applying the percentage of specific constituents against the actual biogas accumulation of the specific samples. For example, the 80M 20V sample was theoretically determined by taking 20 percent of the 100V biogas production and adding it to 80 percent of the 100M biogas production and comparing it to the composite 80M 20V sample. The theoretical biogas production overestimated actual biogas production in all cases. This data is shown in Figure 7.

Figure 7. Theoretical Biogas Production by Percentage vs. Actual Biogas Production



The 80F 20M sample showed the greatest variation while the 80M 20V sample showed the closest correlation. The variation in the 80F 20M sample is most likely attributed to the issues with gas production of the 100F sample due to ripening. This increased gas production was not exhibited by any sample with manure present. This analysis indicates that mixed samples exhibit biogas inhibition most likely due to the varied environment and competition between microbial populations.

CONCLUSION

Methodology to evaluate household waste products for biogas production was established for inclusion into high school science experiments. Variability in COD results show the importance of preparing a uniform sample. COD sampling error was most likely due to large particles clogging the pipette during sample preparation, the dilution procedure, or sample interference with the COD test procedure. Negative COD results for the 100V data did not correlate with biogas production demonstrating that the Hach COD test analysis is not appropriate for spinach samples.

Cummulative biogas production for each sample correlated well with the theoretical biogas production with the exception of the 100V sample (which is explained by the erroneous COD

value assessment). Biogas production was highest for 100F samples due to the banana's ability to produce ethanol and ethyl acetate for ripening. Average biogas production was increased with the amount of manure that was used to seed the sample. However, due to the variability of each sample, the difference in manure seeding rates was not significant.

The methodology presented in this paper offers a way to evaluate household waste products for biogas production for high school science experiments. Following this methodology will allow students to successfully achieving biogas production and obtain a greater understanding of anaerobic digestions as a renewable energy source.

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