

Optimization of Methane Production from Solid Organic Waste

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Abstract

Anaerobic digestion of volatile organic solids (VS) leads to the production of biogas. One constituent of biogas is methane, a clean burning, renewable source of energy. Methane could very well be used to replace typical fossil fuels as our primary energy source. VS are widely available through the collection of manure and other organic wastes.

A significant problem with anaerobic digestion is the long hydraulic retention time (HRT). Typical low-rate digesters require 30-50 day HRT. If biogas production from the digestion of organic solids becomes more efficient, the usage of biogas as an alternative to standard sources of energy will become commonplace.

There are many ways to increase the production of biogas, and in turn, decrease the long HRT. These methods include the use of additives, pretreatment of substrate, and mixing. In this paper, I discuss several methods used to increase biogas production and decrease the hydraulic retention time.

Key Words

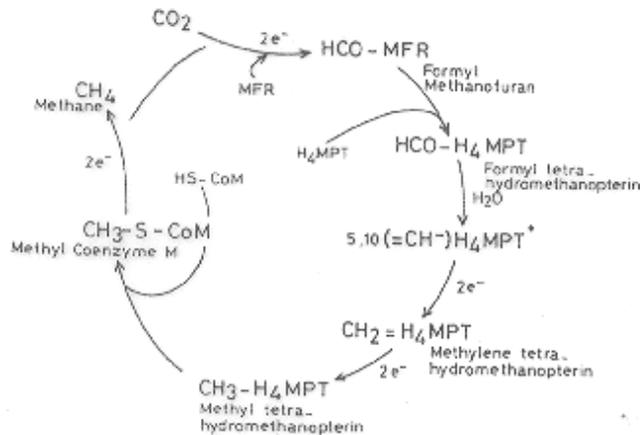
Methane (CH₄), productivity, manure, livestock, methane productivity, volatile solids (VS), volumetric methane production

Introduction

Anaerobic digestion of animal manure results in the production of a biogas composed mainly of methane (CH₄) and carbon dioxide (CO₂). Uncontrolled decomposition of animal manure is undesirable as gases released are believed to have global warming effects. Methane is generated from the digestion of organic compounds in feces, primarily carbohydrates, proteins, and lipids. Methane productivity can be measured in terms of volatile solids (VS) destroyed, VS loaded, volume, or animal production (Moller et al., 2004). In this paper, methane productivity will be discussed chiefly with respect to volume.

Fig. 1 represents the biogas production process by anaerobic respiration. Organic solids are broken down to create methane and carbon dioxide. Taking carbon dioxide, hydrogen from VS is added yielding methane.

Fig. 1 (Nagamani and Ramasamy, 1999)



If anaerobic digestion is managed properly, biogas can be captured and used in place of fossil fuels, providing a CO₂ neutral energy source. In the U.S. and Canada alone, there are over 121 million cattle (USDA). The methane potential from these cattle is 435.6 million m³ per day (Nagamani and Ramasamy, 1999). This equals more than 25% of the average daily consumption of Natural gas in the United States from cattle alone (Energy Information Administration). 1.7 cubic meters of biogas has the energy equivalent of one liter of gasoline. This means that the waste from one cow could generate the equivalent of 200 liters of gasoline in one year (Biogas Production). The long HRT period remains a significant obstacle. The need to improve the overall efficiency of anaerobic digestion exists.

The following table gives the biogas potential from the waste of several different species.

Table 1 (Nagamani and Ramasamy, 1999)

Feedstock	Availability (kg animal ⁻¹ d ⁻¹)	Gas yield (m ³ kg ⁻¹)
Cattle waste	10	0.36
Buffalo waste	15	0.54
Piggery waste	2.25	0.18
Chicken waste	0.18	0.011
Human excreta	0.4	0.028

The factors that affect methane productivity include:

- Species, breed, diet, and maturation stage of the animal
- Amount and type of bedding material
- Type of bacteria selected
- Pretreatment Processes
- Use of mixing techniques
- Separation techniques

In this paper, I will discuss methods that can be used to optimize the production of methane gas using anaerobic digestion of organic waste and decrease the HRT.

Volatile Solids (VS)

A main constituent of manure that can drastically affect the methane productivity during digestion is the volatile organic solids (VS) content. Manures with higher VS ratios will have greater methane productivity. Volumetric methane production can be increased by solid-liquid separation by producing a higher VS concentration. A problem with separation is the liquid portion is high in contaminants and must be treated before releasing to a waterway.

The theoretical methane potential can be calculated from Bushwell's formula. Methane productivity in terms of VS loaded as residence time approaches infinity is referred to as the ultimate methane yield. The ultimate methane yield will always be lower than the theoretical methane yield. If only the solid portion is being used for digestion, it is essential that the separation unit is efficient in transferring VS to the solid fraction because a part of the VS will be present in the liquid (Moller et al., 2004).

Typical VS values vary significantly depending on the source and any pre-treatment. Swine waste contains higher VS concentrations than that of cattle. Sow ($530 \pm 6 \text{ l kg}^{-1}$ VS) waste is generally highest, pigs ($516 \pm 11 \text{ l kg}^{-1}$ VS) are considerably higher than that of cattle manure ($468 \pm 6 \text{ l kg}^{-1}$ VS) (Moller et al., 2004).

As shown above, the methane production does vary slightly depending on the origin of waste, but methane productivity per unit of VS degraded is relatively constant for all waste types. For most livestock the number is around 500 l per kilogram VS. (Hill, 1984).

Additives

Organic and inorganic chemicals can be added to the slurry to improve gas production. Additives can stimulate microbial activity under different operating conditions. Some organic substances are available naturally, but are not much consequence in terms of their use in the habitat. When utilized in biogas production, some additives can greatly improve performance (Yadvika et al. 2004)

Inorganic Additives

There are many inorganic additives that increase gas production. The addition of iron salts has been found to amplify the production of biogas. Salts were added at varying concentrations; FeSO_4 was added at 50 mM, FeCl_3 at $70 \mu\text{M}$ (Clark and Hillman, 1995 as cited by Yadvika et al., 2004). Production facilities with higher concentrations of heavy metals tended to have a greater methane yield than those that did not (Wong and Cheung, 1995). The addition of calcium and magnesium salts as energy supplements improved methane production and avoided foaming of the slurry (Mathiesen, 1989 as cited by Yadvika et al., 2004).

Nickel ions have shown to increase gas production amounts by as much as 54%. Nickel was found to stimulate production up to 5 ppm. The optimum range appeared to be at 2.5 ppm in a water hyacinth-bovine waste substrate. The increased in biogas is due to the activity of nickel dependent metallo-enzymes involved in anaerobic digestion (Geeta et al., 1990).

Other chemicals have significantly enhanced biogas production. Eosin blue dye at a concentration of $0.1 \mu\text{M}$ found a biogas increase of 25-35% when added to manure slurry (Dhawale, 1996). Gaddy discovered a method for improving the performance of anaerobic digestion of solid substrate; at least 1-chelating agent (between $1-100 \mu\text{M}$) and at least one nutrient (between $1-5000 \mu\text{M}$) was added to a solid substrate to make solid nutrients soluble and enhance bacterial growth.

“Methane production can be increased or smaller digesters can be used to achieve the same methane production. Faster start up, greater stability and more rapid recovery from upsets were possible using this new method” (Yadvika et al., 2004).

Organic Additives

Additives can help to maintain conditions that are favorable for more rapid gas production in an anaerobic digester. These conditions include: pH, inhibition/promotion of acetogenesis and methanogenesis, etc. Powdered leaves of some plants have been found to stimulate biogas production between 18-40% (Chowdhry et al., 1994 as cited in Yadvika et al. 2004).

Increased biogas production due to selected additives appears to be due to adsorption of the substrate on the surface of the additives. This can create an increased localized substrate concentration and a more favorable environment for the growth of microbes (Chandra and Gupta 1997).

Plant residues treated with alkali at 1% NaOH for 7 days combined with manure at a 1:1 w/w ratio showed a two fold increase in biogas and methane production (Dar and Tandon, 1987). This method will be discussed in more detail in the “Pretreatment” section of this paper.

Tomato plant waste added to rabbit wastes in quantities greater than 40% improved methane production (Trujillo et al., 1993). Plant waste like corn stalks, rice straw, cotton stalks, wheat straw, and water hyacinth when mixed with cattle manure can increase gas production from 10-80%. Biodegradation of mango processing wastes produced significantly more methane after the addition of bean seeds, black gram, guar, and guar gum at a rate of 1500 ppm.

The addition of organic and inorganic substances to waste slurry increases the efficiency of anaerobic digestion and the production of methane gas. Supplementing manure with leaves and organic residue can increase gas production up to 80%. Most of these options are easy to complete and economically effective.

Pretreatment

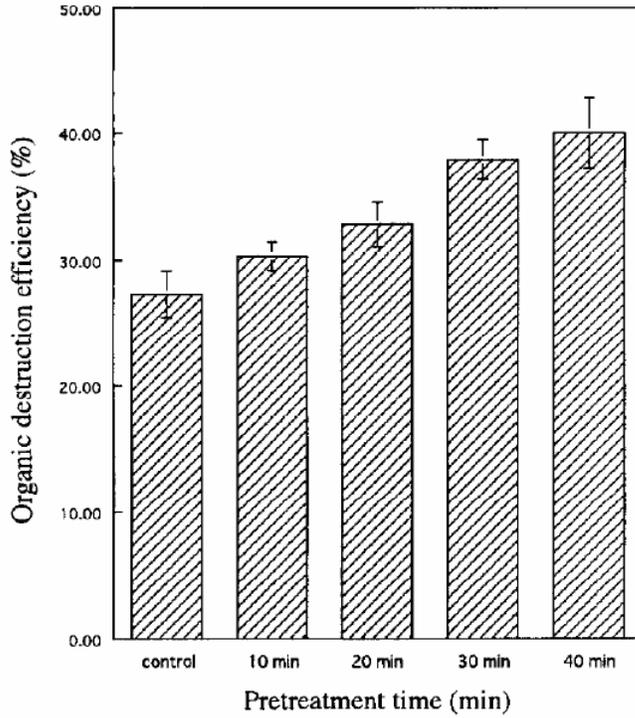
When manure is manipulated prior to entering the digester, this process is called pretreatment. Many pretreatment methods have been tested, and some have shown a significant improvement in terms of biogas and methane production. There are several methods of pretreatment that are quite effective.

Pretreatment of manure by maceration has shown considerable promise to increase the production of biogas. Hartmann, et al., (2000) showed a 25% increase in biogas production when implementing maceration for pretreatment of particulate matter in manure. Maceration appears to increase the surface area of the fibers by separating them and allowing for individual treatment or recirculation. The effects due to shearing, rather than cutting, cause the increased methane productivity. Maceration is a low cost pretreatment option, which provides greater incentive to implement this process for increased biogas production (Hartmann et al., 2000).

Ultrasonic pretreatment of waste activated sludge disrupts cell membranes, resulting in the release of organic substance outside the cell. This allows the substances to be more easily hydrolyzed and improve anaerobic respiration. Methane generation increased with time exposed to ultrasonic pretreatment time. A thirty minute pretreatment resulted in a 64% increase in methane production as compared to control. Thirty minutes is considered the optimum exposure time, as increased exposure time did not result in significant increases in gas production (Wang et al., 1999).

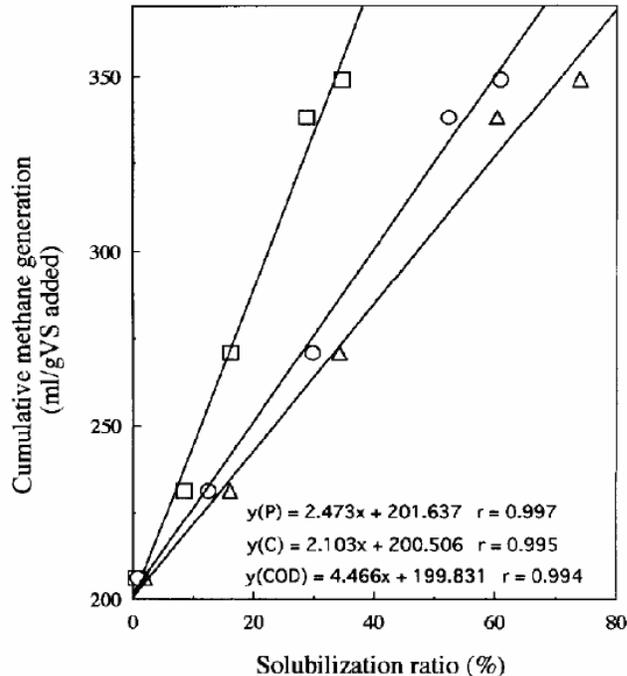
The following figures represent the effect of ultrasonic pretreatment of substrate. Fig. 2 show the destruction of organic matter versus ultrasonic treatment time, and Fig. 3 shows the production of methane versus solubilization ratio. Ultrasonic pretreatment of substrate will increase the solubilization, and in turn increase methane production. The relationships can be seen in the figures below.

Fig. 2 (Wang et al., 1999)



Effect of ultrasonic pretreatment time on the organic destruction efficiency. Standard deviations are represented by error bars.

Fig. 3 (Wang et al., 1999)



The relationship between the solubilization ratio of WAS and methane generation. (○) Protein(P); (△) carbohydrate (C); (□) COD_{Cr}.

Another method that has potential to significantly increase the biogas production is the addition of alkali treated plant residues to cattle manure for 1-2 days (Dar and Tandon 1987). A 200% increase in biogas and methane production was noted. Plant residues were pretreated with a 1% sodium hydroxide (NaOH) solution for one week prior to being mixed with manure. Digestion occurred at room temperature (28-31degrees C). Lantana residue, apple leaf litter, wheat straw, and peach leaf litter were all tested a possible residues. Lantana slurry had the best results with 63-66% of biogas as methane. Efficiency in terms of biogas produced per gram dry matter was 31-42% higher than just cattle manure.

Particle size in substrate will affect the biogas production. The distribution of particle sizes is affected by several factors, which include: animal diet, addition of bulking agents, and pretreatment processes. The particles should not be too large as too clog the digester and inhibit microbial digestion. Smaller particles are desirable. They will have more surface area to adsorb substrate and in turn increase gas production. Particle size can be decreased by pretreatment of waste. Grinding and maceration of substrate are used to achieve smaller particle size and increase gas production (Moller et al., 2002).

Separation techniques were discussed earlier in the paper. Removing water from the solid portion can increase the production of methane by volume of waste. This does not appear to be very effective, as the separated liquid still requires treatment (Moller et al., 2004).

Pretreatment is a key element to enhancing methane generation as it allows for greater accessibility to soluble organic substances. A combination of pretreatment methods appears incompletely researched. The production capacity of a blend of several different pretreatment methods is unknown.

Effects of Temperature

The temperature at which a digester functions has a critical impact on the biogas production process. There are three temperature ranges that select for different bacteria. The psychrophilic range is less than 30 degrees C, mesophilic is between 30-40 degrees C, and thermophilic is between 50 and 60 degrees C. Anaerobic bacteria are most active in the mesophilic and thermophilic range (El-Mashad et al., 2003).

Thermophilic digestion offers many advantages, such as higher metabolic rates and greater specific growth rates. The thermophilic range also provides a high destruction of pathogen and weed seeds, but thermophilic treatment also has drawbacks like lower stability as compared to mesophilic treatment. Thermophilic treatment systems produce lower quality effluent, and a lower growth yield with high growth rates. This leads to a longer startup time and causes the process to be more susceptible to toxicity and changes to operating conditions (El-Mashad et al., 2003).

The following table shows the effluent qualities of both thermophilic and mesophilic bacteria. As shown, the thermophilic effluent is higher in nitrogen (TKN) and ammonia concentrations.

Table 2

TKN and ammonia nitrogen concentrations

System loading g VS/l/day	TKN (NH ₃ -N)		
	Feed	Thermophilic effluent	Mesophilic Effluent
1.87	740 ± 110 (160 ± 50)	660 ± 170 (210 ± 30)	640 ± 120 (330 ± 40)
2.84	1040 ± 160 (220 ± 70)	1000 ± 60 (370 ± 80)	980 ± 70 (500 ± 70)
4.50	1700 ± 90 (340 ± 60)	1630 ± 100 (660 ± 50)	1600 ± 90 (840 ± 60)
5.82	2100 ± 200 (450 ± 50)	2000 ± 150 (750 ± 70)	1950 ± 100 (1090 ± 60)

Table 3 shows the biogas production rates as well as methane produced per gram VS destroyed for thermophilic and mesophilic bacteria. The biogas production is highest with thermophilic bacteria, but the process has several drawbacks.

Table 3 (Harikishan and Sung, 2003)

Methane production rates and conversion efficiencies

Loading g VS/l/day	Biogas thermophilic (l/day)	Biogas mesophilic (l/day)	l CH ₄ /g VS (destroyed)	l CH ₄ /g VS (fed)	l CH ₄ /l reactor vol. (thermophilic)	l CH ₄ /l reactor vol. (mesophilic)
1.87	18.2 ± 1.3	12.7 ± 0.8	0.58	0.22	0.85	0.38
2.84	29.4 ± 1.9	18.2 ± 1.5	0.62	0.23	1.43	0.59
4.50	47.1 ± 2.4	26.1 ± 0.9	0.59	0.23	2.31	0.85
5.82	54.2 ± 1.1	30.0 ± 1.7	0.52	0.21	2.66	1.00

A process patented at Iowa State University by Harikishan and Sung (2003) combines thermophilic and mesophilic digestion. Temperature-phased anaerobic digestion (TPAD) initially operates at high temperatures (around 55 degrees Celsius), and then at mesophilic temperatures (around 35 degrees Celsius) (Harikishan and Sung, 2003).

“By combining the thermophilic and mesophilic digestion process into one, TPAD offers the advantages of both while eliminating the problems associated with these systems independently” (Harikishan and Sung, 2003).

Effect of Mixing

The performance of a digester is highly affected by the degree of contact between substrate and the bacterial population. Contact can be increased by mixing the substrate. Thorough mixing distributes heat and bacteria uniformly in the digester. Mixing is considered essential in large volume anaerobic digesters, but the optimal mixing pattern is still a topic of debate (Karim et al., 2005).

Mixing can be achieved in several different ways. Mechanical mixers, biogas recirculation, and slurry recirculation are three common methods of mixing. Mechanical mixers are considered the most efficient in terms of power used per volume mixed (Karim et al. 2005). The inability to easily access internal fittings and the number of moving parts cause concern with the use of mechanical mixers. For this reason, some sources claim that biogas recirculation is the most efficient method of mixing for anaerobic digestion. Draft tube heights used in biogas recirculation do not appear to have any effect on biogas production (Karim et al., 2005).

Another technique used to mix slurry is the recirculation of digested slurry. This method has shown improvements on gas production similar to that of biogas recirculation. Reintroduction of digested substrate back into the slurry allows microbes that had been washed away back into the digester, increasing the microbial population (Yadvika et al., 2004).

More homogeneous slurry can also be attained by feeding slurry into the digester with reduced loading rate, instead of more lengthy periodic additions. This method can provide the same mixing effects with less need for mechanical operation. This method is more cumbersome, and requires greater interaction with the digester units. For this reason, it does not appear to be feasible in larger facilities (Mohanrao, 1974 as cited by Yadvika et al., 2004).

Agitation of the slurry substrate is necessary to ensure a uniform mixture of heat and bacteria within an anaerobic digester. Mixing can be attained by mechanical mixers, biogas recirculation, and frequent addition of substrate to the mixture as well as several other methods. Mixing evenly distributes slurry components and prevents dead zones within substrate. With large volume reactors, mixing is a necessity.

The following figures represent the effectiveness of the four different methods of mixing that were tested. The results show that a digester with 15% feed manure in slurry with recirculation of biogas had the highest biogas production rates. In all cases, independent of feed manure percentage, biogas recirculation showed the highest biogas production rates.

Table 4 (Karim et al., 2005)

Operational conditions for the digesters

Experiment set	Digester	Mode of mixing	Feed manure slurry (%)
1	1	Unmixed	5
	2	Biogas-mixed	5
	3	Impeller-mixed	5
	4	Slurry recirculation	5
2	5	Unmixed	10
	6	Biogas-mixed	10
	7	Impeller-mixed	10
	8	Slurry recirculation	10
3	9	Unmixed	15
	10	Biogas-mixed	15
	11	Impeller-mixed	15

Table 5 (Karim et al., 2005)

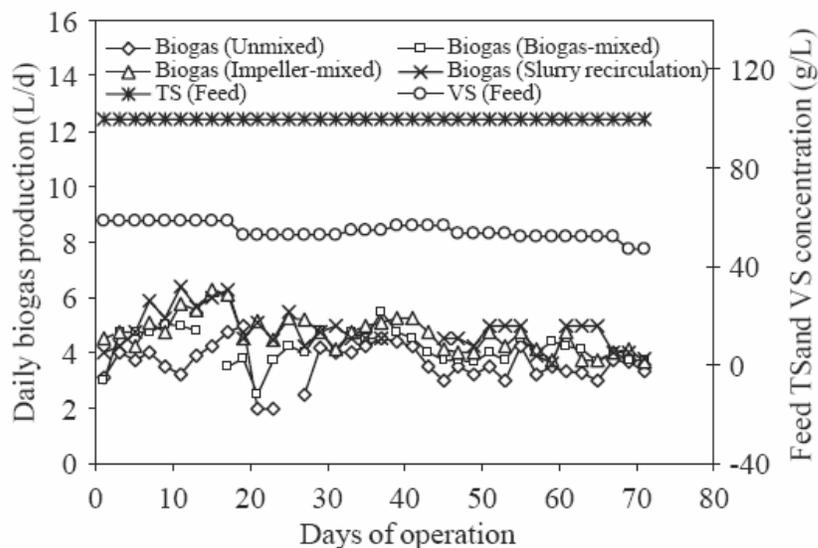
Average biogas production rate and methane yield for the digesters over the last 30 days of operation

Set of expt.	Digester	Mode of mixing	VS loading (g/L d)	^a Biogas production rate (L/L/d)	Methane yield (L CH ₄ /g VS loaded)	^b Statistical significance
1	1	Unmixed	2	0.84 ± 0.07	0.27	A
	2	Biogas-mixed	2	0.94 ± 0.07	0.26	A
	3	Impeller-mixed	2	0.88 ± 0.09	0.27	A
	4	Slurry recirculation	2	0.85 ± 0.09	0.28	A
2	5	Unmixed	3.24	0.92 ± 0.1	0.19	B
	6	Biogas-mixed	3.24	1.07 ± 0.08	0.21	C
	7	Impeller-mixed	3.24	1.14 ± 0.13	0.23	D
	8	Slurry recirculation	3.24	1.20 ± 0.14	0.24	D
3	9	Unmixed	3.24	1.13 ± 0.14	0.15	E
	10	Biogas-mixed	3.24	1.64 ± 0.32	0.23	F
	11	Impeller-mixed	3.24	1.25 ± 0.12	0.17	F

^a ± shows the standard error

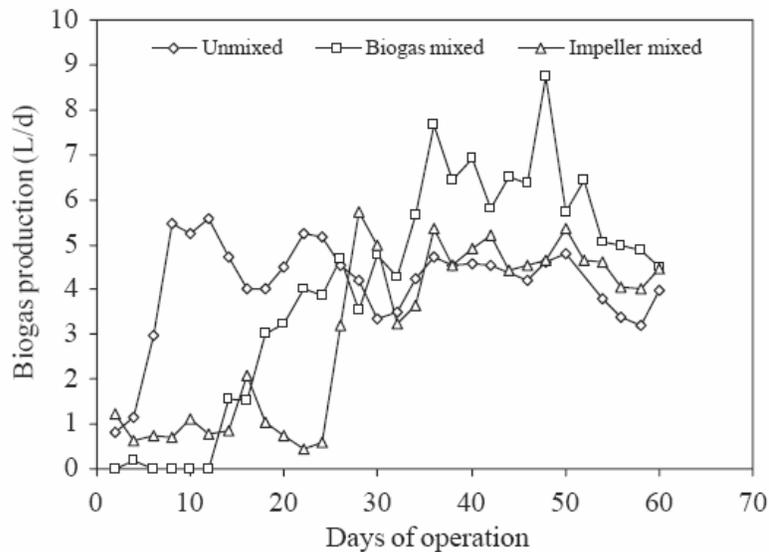
^b Alphabetic symbols given in the last column depict statistically same/different performance of the digesters. Please note that the analysis of variance (ANOVA) was performed separately for each of the three sets of experiments.

Fig. 4 (Karim et al., 2005)



Daily biogas production from Digesters 5–8 along with the TS and VS concentrations in the 10% feed slurry study.

Fig. 5 (Karim et al., 2005)



Daily biogas production for Digesters 9–11 during the 15% feed slurry study.

Type of Bacteria Selected

In an anaerobic digester, it is possible to create conditions that will promote the growth of specific types of bacteria. This is called selecting for those bacteria. Varying conditions such as pH and temperature will select for different organisms. Certain strains of bacteria will increase methane and biogas production by stimulating certain enzymes. Bacterial strains that digest cellulose, such as actinomycetes and mixed consortia can improve biogas production from 8.4-44% (Yadvika et al., 2004).

Temperature

Bacteria associated with anaerobic sludge digestion perform best in the mesophilic and thermophilic temperature ranges. (Yadvika et al., 2004). Creating the proper conditions for optimal bacterial growth is essential to optimizing bacterial growth. Thermophilic methanogens have higher biogas production rates, but they are often less appealing. Thermophiles deliver a lower quality effluent and frequently require energy to maintain the higher temperatures. For this reason, mesophilic digestion is more common (Harikishan and Sung, 2003).

Carbon/Nitrogen Ratio

Carbon is used as an energy source during anaerobic respiration, and for this reason microbes require a higher carbon demand. Bacteria necessitate a 30:1 Carbon to Nitrogen ratio with a majority of the carbon available for anaerobic respiration (Bardiya and Gaur, 1997 as cited by Yadvika et al., 2004). Carbon to nitrogen ratios can be varied by the addition of materials high in the desired compound. By adding urine to cow manure researchers were able to attain nearly twice the biogas from an equivalent amount of manure. The process was especially beneficial during the coldest months of the year when production is lowest (Idnani and Laura, 1971 as cited by Yadvika et al., 2004)

Role of pH

pH plays an important role when considering the growth of microbial life during digestion. Anaerobes prefer a pH close to neutral, in the range of 6.8-7.2. The amount of carbon dioxide

and VS produced during digestion affects the pH of the substrate. Carbon dioxide can create acetic acid and lower the pH of the slurry. For anaerobic digestion to continue, the acetic acid concentration must be below 2000 mg/l (Yadvika et al., 2004).

Origin of Waste

All organic material, including food and yard wastes can be decomposed to generate biogas and methane. Waste from different sources will have highly variable biogas production mostly due to varying VS concentrations. Methane production varies between animal species and by the diet, breed, and maturation stage (Giger-Reverdin et al., 2002).

Giger and Morand (2002) found that waste with higher ether levels produced more gas. Ether is composed of fatty acid and unsaponified parts. Methane generation is a function of only the fatty acid part (Giger-Reverdin et al., 2002).

Pig and sow tend to have higher theoretical methane production than that of cattle. Sow show the highest gas production which is slightly higher than that of pig. Cattle have significantly lower production volumes. This discrepancy is likely due to the proportion of lipid in manure. Lipid is much higher in swine than cattle due to diet. Cattle are fed roughage which is higher in lignin as compared to swine feed (Giger-Reverdin et al., 2002).

Conclusion

The use of anaerobic digestion of organic waste to produce biogas has the ability to replace fossil fuels as our primary energy source. The main constituents of biogas are carbon dioxide and methane. Methane is a carbon neutral energy source that burns cleanly to produce carbon dioxide and water. With hundreds of millions of cattle and swine worldwide, the methane potential is colossal.

The main drawback of anaerobic production is the long hydraulic retention time. With methane optimization techniques, biogas production rates can be significantly increased and the hydraulic retention time can be decreased. The methods to optimize production that have been discussed in this paper have given viability to anaerobic digestion as a renewable, non-polluting energy source.

The need of further research still exists for methane optimization. How a combination of several processes affects methane production remains largely unresearched. Combining several of the most promising practices, such as ultrasonic pretreatment combined with additives and biogas recirculation could drastically increase biogas production and decrease the hydraulic retention time. For biogas to compete with fossil fuels as a viable energy source, researchers must find ways to increase efficiency in the production process. Anaerobic digestion of organic wastes is a sustainable practice to produce a clean burning, carbon neutral energy source, but the process must first be refined.

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