Anaerobic Digestion of Animal Manures: Understanding the Basic Processes

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Biological Process

The process of producing methane from manure is fairly straight forward—seal manure in an airtight container and it will form biogas, which is a mixture of methane (CH_4), carbon dioxide (CO_2) and trace amounts of other gases. However, behind the apparent simplicity, lie complicated interactions involving several communities of microorganisms.

Anaerobic digestion is a multi-stage process (Figure 1) involving two to four steps, depending on where you want to draw lines in the process. Communities of hydrolytic bacteria break complex organic matter down to simpler compounds. Acid forming bacteria convert the simple compounds to volatile fatty acids—principally acetic acid, or vinegar. Hydrolysis and acidosis are commonly lumped together and called anaerobic fermentation. Some microbiologists also distinguish between formation of mixed volatile fatty acids (acidosis) and reduction to acetic acid (acetogenesis).

Methanogens are methane forming microorganisms that belong to the Archaea domain—very simple, single cell organisms similar to bacteria. Methanogens take the end products of fermentation—volatile fatty acids, hydrogen gas (H_2), CO_2, and water (H_2O)—and use them to form methane. Methanogens fall into two main camps depending on the pathway they use to produce methane (Figure 2). All methanogens can reduce CO_2 and H_2 into CH_4 and H_2O; those that use this pathway exclusively are called hydrotrophic methanogens. Methanogens that convert volatile fatty acids and a number of other simple organic compounds to CH_4 and CO_2 are called acetotrophic methanogens.

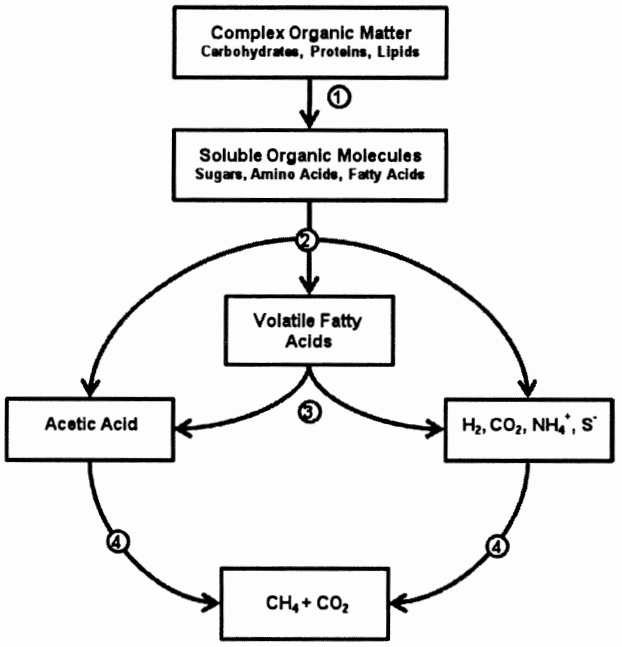


Figure 1. Steps in anaerobic digestion.

Acetic acid Cleavage

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Carbon dioxide Reduction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Figure 2. Major pathways of methane formation.

Limitations on Biological Processes

Anaerobic digestion is a living process, and like all biological communities, the microorganisms that carry out anaerobic fermentation and methanogensis, do so under certain operating conditions.

Time and Space to Grow

All communities of organisms such as methanogens and human beings grow in a pattern similar to the one shown in Figure 3, if given an ample food supply, sufficient room to expand, and have the absence of predators or competing organisms. The lag time occurs as the organisms acclimate to their environment. During the growth phase, food is not limiting and population expands rapidly. Sometimes the growth phase is called the log growth or exponential growth phase because the growth pattern follows an exponential curve. Population growth slows in the decline phase as the organisms meet the limit of their food supply. During the stationary phase, the community has met the limits of its food supply. Bear in mind that reproduction does not necessarily stop during the decline and stationary phases—the death rate approaches the reproduction rate. In some cases the community becomes dormant or goes into hibernation during the stationary phase. Communities enter a death or endogenous growth phase once

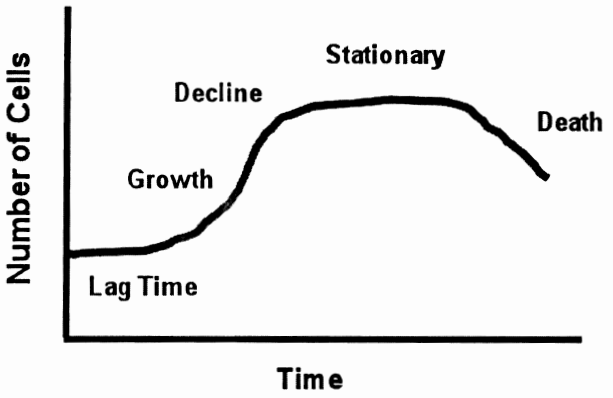


Figure 3. Generalized microbial growth curve.

a limited food supply is exhausted or an inhibiting element limits the further growth of organisms. During endogenous growth, the death rate exceeds the birth rate.

The inhibitory elements that cause endogenous growth are often the end products of a community's metabolism. The beauty of anaerobic digestion is that it is the work of a mixed community of organisms. The toxic end product of one community is the food supply of another. Acid forming bacteria consume the simple sugars that might inhibit hydrolytic communities. Methanogens use the acids formed in fermentation to produce CH_4 and CO_2. And in the end, CH_4 and CO_2 leave the digester as biogas.

Reproduction Time

Most anaerobic digesters are designed so that the microbial communities remain in exponential growth. An important concept to grasp is the doubling rate or reproduction time of an organism. This is the time needed for a population to double in size during exponential growth. In simple terms it is the time required for the organisms to replace themselves.

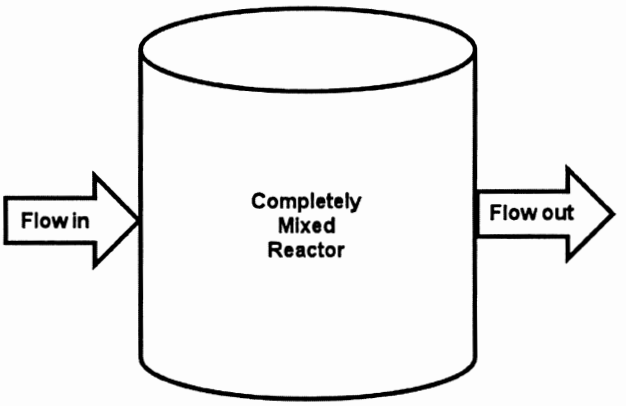
Hydraulic Retention Time

Anaerobic digestion generally takes place in a liquid, continuous flow reactor (Figure 4). If the reactor volume does not change, then outflow of the reactor equals flow into the reactor, and the average time the liquid remains in the reactor is its volume divided by the flow rate. This is called the hydraulic retention time of the reactor, abbreviated as HRT.

If the reactor is completely mixed—the microorganisms are completely suspended in the reactor—then the time the cells remain in the reactor equals the HRT. If the HRT of a completely mixed reactor equals the reproduction time of the organisms living in the rector, a new cell is formed to replace each cell leaving the reactor, and the population within the reactor remains stable. If the HRT is shorter than the reproduction time, a new cell will not be there to replace the one leaving, and the population will decline or wash out.

Solids Retention Time

Reducing HRT decreases reactor size, and smaller reactors reduce costs. Therefore, many digestion systems are designed so microorganisms remain in the reactor longer than its HRT. For instance, we could put a screen on the outlet of the reactor in Figure 4 so some of the microorganisms are trapped inside. We can calculate cell retention time by



If Flow in = Flow out

$$HRT = \frac{\text{Reactor Volume}}{\text{Flow out}}$$

$$SRT = \frac{\text{Mass of Solids in Reactor}}{\text{Mass of Solids Leaving}}$$

Figure 4. Relationships among reactor volume, flow, solids mass and retention times in a completely mixed reactor.

dividing the mass of microorganisms trapped in the reactor by the mass of organisms leaving the reactor. The microbial population is kept stable by setting cell retention time equal to reproduction time.

It is easier to measure the total mass of solid particles suspended in liquid rather than only the mass of viable cells. Therefore, cell retention time is approximated by solids retention time—or SRT— the mass of solids in the reactor divided by the mass of solids leaving.

Steady Food Supply

Microorganisms need food to reproduce and grow. Methanogens have the uncanny ability to go dormant during periods of food shortage. This is good because you can easily restart an anaerobic digester after long periods of inactivity. On the other hand, sudden increases in feeding can cause bursts of gas production, which leads to foaming and scum formation in the digester.

Temperature

Methanogens thrive in two temperature ranges. Thermophyllic (heat loving) methanogens are fast growing with a reproduction time of 10 to 15 days, but they operate in a fairly narrow band of temperature centered on 55 C. Mesophyllic methanogens are slower growing with a reproduction time of up to 30 days, but they tolerate a wider range of temperatures. 35 C is optimal for mesophyllic methanogens, but they can tolerate much lower temperatures. Provided they have sufficiently long SRT, digesters operated at 20 C do not show substantial loses in gas production when compared to those operated at 35 C.

Oxygen

Methanogens are strict anaerobes, meaning the least amount of oxygen is poison to them. Acid forming bacteria are

more tolerant of oxygen. So, if oxygen gets into an anaerobic digester, methane concentration will drop and carbon dioxide concentration will increase in the biogas.

pH

A major indicator of reactor health is pH. A complex set of naturally occurring buffers control pH within an anaerobic digester, with organic acid-ammonia and carbonate-bicarbonate being the most important buffers. The optimum pH range for anaerobic digestion is neutral to slightly basic—a pH of 6.6 to 7.6.

Inhibitory Substances Commonly Found in Manure

Inhibiting elements are often called toxic, but toxicity is a misnomer. Low doses of most inhibitory agents actually stimulate biological activity. The following four sets of chemicals are the major inhibitory agents found in animal manures.

Antibiotics

Antibiotics given therapeutically or fed sub-therapeutically to animals have the potential to alter the communities of microorganisms digesting manure from treated animals. The inhibitory effect of antibiotics on gas production has been shown to be minimal if high SRT is maintained and the microorganisms are given time to acclimate.

Ammonia

Ammonium ion (NH_4^+) and its gaseous relative, Ammonia (NH_3), are byproducts of protein digestion and reduction of urea. Concentrations at which Ammonical Nitrogen ($NH_4^+NH_3$-N) are beneficial, inhibitory or toxic to anaerobic digestion are given in Table 1. The toxicity of ammonia is highly dependent on pH. NH_3, which is the predominant form at higher pH, is more toxic than NH_4^+. Usually, ammonia is not a problem in manure digesters, except for reactors treating highly nitrogenous materials such as poultry manure. Some poultry manure digesters have been able to tolerate levels as high as 6,000 mg/l if the microorganisms are given time to acclimate.

Table 1. Effect of ammonia and sulfide concentrations on anaerobic treatments.

Effect on Anaerobic Treatment	*$NH_4^+NH_3$-N mg/l*	*S^- mg/l*
Beneficial	50 – 200	< 50
No Adverse Effect	200 – 1,000	50 – 100
Inhibitory at higher pH values	1,500 – 3,000	100 – 200
Toxic	> 3,000	> 200

Sulfate and Sulfide

Sulfate (SO_4^-) is not an inhibitory substance, per se. Its presence can reduce CH_4 production because a group of bacteria called sulfate reducers can out compete hydrotrophic methanogens for available H_2. Competition with sulfate reducers does not usually reduce production from manure digesters since there is plenty of acetic acid around for acetotrophic methanogens to produce gas. The end product of sulfate reduction, Sulfide (S^-), can be quite toxic to anaerobic digestion. Like ammonia, the toxicity of S^- is dependent on digester pH. Stimulatory and inhibitory concentrations of sulfide are given in Table 1. Also, like ammonia, S^- exists in a gaseous form—hydrogen sulfide (H_2S)—so its control is a balance between source reduction, gas production and pH.

Salt

The higher the soluble salt content in a digester, the harder microorganisms have to work to transport water in and out of their cells. Research has shown it is mainly the cations (positive ions in solution) that inhibit microbial activity. Stimulatory and inhibitory concentrations of base cations are given in Table 2.

Precipitation of Inhibitory Substances

It should be noted that most inhibitory substances must be in solution to reduce biological activity in digesters. Therefore, the inhibitory effect of S^- is reduced through precipitation of insoluble metal sulfides. Soluble Mg and NH_3 are reduced by precipitation of Struvite ($MgNH_4PO_4$).

Table 2. Stimulatory and inhibitory concentrations of base cations.

Cation	*Concentration, mg/l*		
	Stimulatory	*Moderately Inhibitory*	*Strongly Inhibitory*
Sodium, Na^+	100 – 200	3,500 – 5,500	8,000
Potassium, K^+	200 – 400	2,500 – 4,500	12,000
Calcium, Ca^{+2}	100 – 200	2,500 – 4,500	8,000
Magnesium, Mg^+	75 – 150	1,000 – 1,500	3,000

Upset Conditions and Their Control

Fermentative bacteria are generally more robust and faster growing than methanogens. The first indication that something is wrong with a digester occurs when the acid formers start to over power the methane formers. This may show up as a drop in biogas production. But, even before gas prduction drops, the CO_2 concentration in the biogas increases and the organic acid concentration of the reactor liquid increases. Both of these will cause a drop in pH. So, daily measurement of pH is a good method to monitor digester health. The relationship between fermentative and methanogenic communities can become so unbalanced that even the acid formers can no longer tolerate the low pH conditions. At this point we say the digester is stuck, or has soured or become pickled.

Basic steps to follow in case of digester upset are:

1. Reduce the feeding rate.
2. Stabilize pH.
3. Determine and correct the cause of the imbalance.
4. Slowly increase the feeding rate while maintaining neutral pH.

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