Anaerobic digestion (AD) is the process of microbial decomposition of organic substances in the absence of oxygen. The biogas produced by AD is composed of methane (50-80%), carbon dioxide (20-50%), and trace levels of water vapor and other gases, such as hydrogen sulfide ($H_2S$).

$H_2S$ is toxic to humans and corrosive to biogas plumbing and utilization equipment. A concentration of 100 ppm is considered immediately dangerous to life and health by the National Institute for Occupational Safety and Health (NIOSH). Even at low levels (100 ppm), $H_2S$ can cause negative health effects, such as nausea, headaches, and breathing problems, while at higher levels (> 300 ppm), it can cause suffocation.

$H_2S$ is toxic and reactive with metals and cement and is readily converted into $SO_2$ and $H_2SO_4$, which are also highly corrosive. In addition, combustion of $H_2S$ in gas engine generators forms sulfur dioxide ($SO_2$). The produced $SO_2$ can react with water vapor in biogas to form sulfuric acid, which acidifies the engine oil and can corrode the engine, if the acidic oil is not changed frequently. Due to the toxicity and adverse effects of $H_2S$ to humans and equipment, it is beneficial to remove $H_2S$ from biogas.

One simple method to remove $H_2S$ contamination in biogas (known as desulfurization) is controlled addition of oxygen (air) into the headspace of an AD unit to create a microaerobic environment (Figure 1). A microaerobic environment is used as a biological $H_2S$ removal method where sulfur oxidizing bacteria (SOB), already present in the digester, use $H_2S$ and $O_2$ as an energy source. This results in the production of elemental sulfur as the end-product instead of $H_2S$ in the biogas. This biological desulfurization process does not require chemicals or water inputs, which can be costly to purchase, in addition to the time and cost associated with properly managing the purchasing and disposal of any chemical additions.

In microaeration, a regulated amount of $O_2$, between 0.3 to 3% of produced biogas, is injected into the digester to create a microaerobic environment. Normally, air (21% oxygen, 79% nitrogen) is used to provide this $O_2$ source, resulting in an air dosage range of 1.5% to 15% of produced biogas to create the desired $O_2$ concentration. This is a variable range because the airflow rate needed to convert $H_2S$ to elemental sulfur is dependent on both the sulfur concentrations in the feedstock and the biogas production rate.

A properly controlled microaerobic environment can remove $H_2S$ without large reductions in biogas.
production and quality. In this case, elemental sulfur (S\(^0\)) is produced when \(O_2\) concentration is limited within a microaerobic environment (Equation 1 in Figure 2)\(^3,7\). When oxygen is present in higher concentrations, the reaction between \(H_2S\) and \(O_2\) creates sulfate (\(SO_4^{2-}\)) as an end-product (Equation 2 in Figure 2).

\[
\begin{align*}
(1) \quad & H_2S + \frac{1}{2} O_2 \rightarrow S^0 + H_2O \\
(2) \quad & H_2S + 2 O_2 \rightarrow SO_4^{2-} + 2H^+ \\
\end{align*}
\]

**Figure 2: Equations between sulfur and oxygen\(^8\).**

The controlled microaerobic environment causes elemental sulfur to accumulate on the walls and the headspace of the digester where SOB grow, as seen in Figure 3. If too much sulfur builds-up, \(H_2S\) removal efficiency may decrease due to decreased biogas residence time and \(O_2\) transfer rates\(^5\). When removal efficiencies significantly drop, the \(S^0\) build-up needs to be removed to help increase \(H_2S\) removal. The removal usually requires the removal of the digester top, which can be expensive and result in increased digester downtime.

**Figure 3: Accumulation of elemental sulfur on the walls and headspace of digester\(^6\).**

**Air vs. Oxygen**

Air or pure oxygen can be used for in-situ microaeration with similar removal rates of \(H_2S\). Air is more often used, as it is free to use, while pure oxygen must be purchased. However, because air contains 79% inert nitrogen (\(N_2\)), the use of air can undesirably dilute the biogas\(^3\). Lower methane percentages from the dilution may adversely affect generator performance for electricity production. Therefore, when the goal is to create high quality biogas, such as renewable natural gas (RNG), oxygen may be preferred to eliminate \(N_2\) dilution with air injection.

**Headspace vs. Recirculation**

Oxygen (or air) can be introduced directly into the headspace and/or the liquid phase with an air pump. If biogas is used for mixing the liquid phase in the digester, air can also be injected directly into the biogas during recirculation\(^5\). Adding air into a recirculation system, with either biogas or sludge recirculation, helps to remove sulfur in the liquid phase, reducing competition for the organic matter between sulfur oxidizing bacteria and methane producing bacteria. The reduced competition can help to increase methane production\(^3\).

Research has shown \(H_2S\) removal by SOB occurs mainly in the headspace and gas-liquid interface, where most SOB live\(^3\). When air is injected into the sludge layer sludge, higher air flow rates are often needed because \(O_2\) may also react with other aerobic bacteria to break down organic compounds. The higher air flow needed for \(H_2S\) removal may increase the biogas dilution due to the increased \(N_2\) addition.

**Airflow Control**

Sulfur concentrations entering the digester vary due to changing sulfur concentrations in the feedstock, which affects \(H_2S\) concentration. The \(O_2\) flow should be controlled to match changing sulfur feedstock concentrations. A handheld gas analyzer can be used to monitor biogas composition (\(CH_4, CO_2, O_2\), and \(H_2S\)) and the information used to adjust air flow into the AD headspace. Maintaining oxygen levels between 0.3% and 0.5% will keep \(H_2S\) concentrations between 100 and 500 ppm\(^9\). While air injection does decrease \(CH_4\) and \(CO_2\) concentrations in the biogas with increasing air additions due to \(N_2\) addition, studies have shown that when the \(O_2\) concentrations was less than or equal to 1% \(O_2\) there was no apparent effect from aeration on the \(CH_4\) production rate\(^9\).

One microaeration control method is a proportional integral derivative controller, which automatically adjusts the air flow rate to match biogas sulfide...
content by measuring the sulfide concentrations in the biogas. This control method, while effective, can increase the capital costs of the microaeration system.

It is important to be aware that overdosing of air can be a safety issue. Too much \( O_2 \) in biogas can result in an explosive mixture. Concentrations need to remain below the range of 6% to 12% \( O_2 \) when the methane concentration is equal to or greater than 60% \( CH_4 \). If airflow control mechanisms on the air pump stop working, or are not installed, and too much air enters the digestion headspace, there is a potential for an explosive mixture to occur.

More Information:

For more information, contact your local agricultural extension agent or visit the Cooperative Extension System website at: www.extension.umd.org.

Additional Contacts:

Dr. Stephanie Lansing (UMD): slansing@umd.edu
Dr. Gary Felton (UMD): gfelton@umd.edu

References:


Authors: Margaret A. Hines, Abhinav Choudhury, Gary Felton and Stephanie A. Lansing

This publication, Title (FS-xxxx), is a series of publications of the University of Maryland Extension and the Department of Environmental Science and Technology. The information presented has met UME peer review standards, including internal and external technical review. For more information on related publications and programs, visit http://www.csst.umd.edu. Please visit http://extension.umd.edu/ to find out more about Extension programs in Maryland.

Issued in furtherance of Cooperative Extension work, acts of May 8 and June 30, 1914, in cooperation with the U.S. Department of Agriculture, University of Maryland, College Park, and local governments. Chang's Wei, Director of University of Maryland Extension.

The University of Maryland is equal opportunity. The University’s policies, programs, and activities are in conformance with pertinent Federal and State laws and regulations on nondiscrimination regarding race, color, religion, age, national origin, gender, sexual orientation, marital or parental status, or disability. Inquiries regarding compliance with Title VI of the Civil Rights Act of 1964, as amended; Title IX of the Educational Amendment; Section 504 of the Rehabilitation Act of 1973; and the Americans With Disabilities Act of 1990, or related legal requirements should be directed to the Director of Human Resources Management, Office of the Dean, College of Agriculture and Natural Resources, Systems Hall, College Park, MD 20742.

For more information on this and other topics visit the University of Maryland Extension website at www.extension.umd.edu