Micro-aeration for Hydrogen Sulfide Removal in Biogas

Introduction

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 (H₂S).

H₂S 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), H₂S can cause negative health effects, such as nausea, headaches, and breathing problems, while at higher levels (> 300 ppm), it can cause suffocation.

H₂S is toxic and reactive with metals and cement and is readily converted into SO₂ and H₂SO₄, which are also highly corrosive. In addition, combustion of H₂S in gas engine generators forms sulfur dioxide (SO₂). The produced SO₂ 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 H₂S to humans and equipment, it is beneficial to remove H₂S from biogas.

One simple method to remove H₂S 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 H₂S removal method where sulfur oxidizing bacteria (SOB), already present in the digester, use H₂S and O₂ as an energy source. This results in the production of elemental sulfur as the end-product instead of H₂S 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-situ Micro-aeration

In micro-aeration, a regulated amount of O₂, 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 O₂ source, resulting in an air dosage range of 1.5% to 15% of produced biogas to create the desired O₂ concentration. This is a variable range because the airflow rate needed to convert H₂S to elemental sulfur is dependent on both the sulfur concentrations in the feedstock and the biogas production rate.

Figure 1: A basic representation of In-situ micro-aeration.
A properly controlled microaerobic environment can remove H₂S without large reductions in biogas production and quality. In this case, elemental sulfur (S⁰) is produced when O₂ concentration is limited within a microaerobic environment (Equation 1 in Figure 2)³⁷. When oxygen is present in higher concentrations, the reaction between H₂S and O₂ creates sulfate (SO₄²⁻) as an end-product (Equation 2 in Figure 2).

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\begin{align*}
(1) \quad & \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S}^0 + \text{H}_2\text{O} \\
(2) \quad & \text{H}_2\text{S} + 2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+
\end{align*}
\]

**Figure 2:** Equations between sulfur and oxygen⁸.

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, H₂S removal efficiency may decrease due to decreased biogas residence time and O₂ transfer rates⁵. When removal efficiencies significantly drop, the S⁰ build-up needs to be removed to help increase H₂S 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 digester⁶.

**Air vs. Oxygen**

Air or pure oxygen can be used for in-situ micro-aeration with similar removal rates of H₂S. Air is more often used, as it is free to use, while pure oxygen must be purchased. However, because air contains 79% inert nitrogen (N₂), the use of air can undesirably dilute the biogas³. 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 N₂ 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 recirculation⁵. 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 production³.

Research has shown H₂S removal by SOB occurs mainly in the headspace and gas-liquid interface, where most SOB live³. When air is injected into the sludge layer sludge, higher air flow rates are often needed because O₂ may also react with other aerobic bacteria to break down organic compounds. The higher air flow needed for H₂S removal may increase the biogas dilution due to the increased N₂ addition.

**Airflow Control**

Sulfur concentrations entering the digester vary due to changing sulfur concentrations in the feedstock, which affects H₂S concentration. The O₂ flow should be controlled to match changing sulfur feedstock concentrations. A handheld gas analyzer can be used to monitor biogas composition (CH₄, CO₂, O₂, and H₂S) and the information used to adjust air flow into the AD headspace. Maintaining oxygen levels between 0.3% and 0.5% will keep H₂S concentrations between 100 and 500 ppm⁹. While air injection does decrease CH₄ and CO₂ concentrations in the biogas with increasing air additions due to N₂ addition, studies have shown that when the O₂ concentrations was less than or equal to 1% O₂ there was no apparent effect from aeration on the CH₄ production rate⁹.
One micro-aeration 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\textsuperscript{10}. This control method, while effective, can increase the capital costs of the micro-aeration system.

It is important to be aware that overdosing of air can be a safety issue. Too much O\textsubscript{2} in biogas can result in an explosive mixture. Concentrations need to remain below the range of 6\% to 12\% O\textsubscript{2} when the methane concentration is equal to or greater than 60\% CH\textsubscript{4}\textsuperscript{11}. 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.edu

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