

Microaeration 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)¹. 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 suffocation¹.

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 biogas².

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 source³. 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 additions⁴.

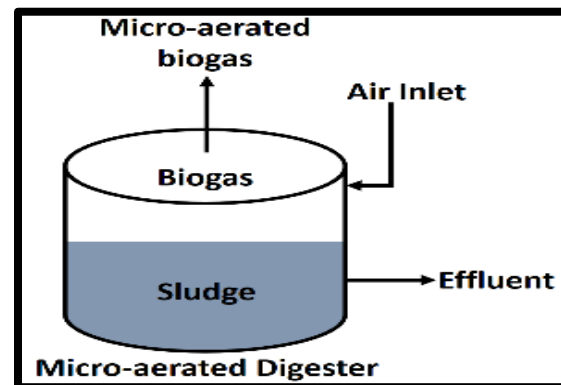


Figure 1: A basic representation of In-situ microaeration.

In-situ Microaeration

In microaeration, a regulated amount of O₂, between 0.3 to 3% of produced biogas, is injected into the digester to create a microaerobic environment³. 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.

A properly controlled microaerobic environment can remove H₂S 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).

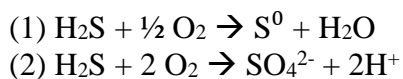


Figure 2: Equations between sulfur and oxygen⁸.

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, H_2S removal efficiency may decrease due to decreased biogas residence time and O_2 transfer rates⁵. 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 digester⁶.

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 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 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 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 H_2S 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 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 ppm⁹. 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 rate⁹.

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 biogas¹⁰. 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 O₂ in biogas can result in an explosive mixture. Concentrations need to remain below the range of 6% to 12% O₂ when the methane concentration is equal to or greater than 60% CH₄¹¹. 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:

1. United States Department of Labor- OSHA. Hydrogen Sulfide – Hazards. Available at: www.osha.gov/SLTC/hydrogensulfide/hazards.html.
2. Kronos Ecochem. 2014. Hydrogen sulfide elimination from biogas.
3. Krayzelova, L., Bartacek, J., Díaz, I., Jeison, D., Volcke, E. I. P., & Jenicke, P. 2015, Microaeration for hydrogen sulfide removal during anaerobic treatment: a review. *Reviews in Environmental Science and Technology*. 14:703-725.
4. Syed, M., Soreanu, G., Falletta, P., and Béland, M. 2006. Removal of hydrogen sulfide from gas streams using biological processes – a review. *Canadian Biosystems Engineering*. 48: 2.1-2.14.
5. Muñoz R, Meier L, Diaz I, Jeison D. 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Reviews in Environmental Science and Bio/Technology*. 14: 727-59.
6. Díaz, I. and Fdz-Polanco, M. 2012. Robustness of the microaerobic removal of hydrogen sulfide from biogas. *Water Science & Technology*. 65(8): 1368-1374.
7. Duangmanee, T. 2009. Micro-aeration for hydrogen sulfide removal from biogas. Iowa State University Graduate Theses and Dissertations.
8. Díaz, I., Pérez, S.I., Ferrero, E.M., and Fdz-Polanco, M. 2011. Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters. *Bioresource Technology*. 102: 3768-3775.
9. Mulbry, W., Lansing, S., Selmer, K., 2017. Effect of liquid surface area on hydrogen sulfide oxidation during microaeration in dairy manure digesters. *PLoS One* 12(10): e0185738.
10. Ramos, I. and Fdz-Polanco. 2014. Microaerobic control of biogas sulphide content during sewage sludge digestion by using biogas production and hydrogen sulphide concentration. *Chemical Engineering Journal*. 250: 303-311.
11. Wellinger A., and Lindberg A. 2000. Biogas upgrading and utilization. IEA Bionergy. Task 24.

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.enst.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. Cheng-i 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 Amendments; 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, Symons Hall, College Park, MD 20742.