

<u>HYDROGEN SULFIDE REMOVAL FROM BIOGAS</u> Part 2C: Biotrickling filters for H₂S – Improvement opportunities

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Controls and innovative processes to improve the performance of biotrickling filter (BTF) and the oxidation of H_2S to sulfate by sulfur oxidizing bacteria (SOB) are summarized below.

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BIOGAS LOADING, RESIDENCE TIME & BTF VESSEL SIZE

Empty bed residence times for BTF at NYS farms are 7-8 min.. While within the acceptable range $(2-16 \text{ min.})^{[2]}$, these EBRT are slower than many high performing systems where EBRT is $< 1 \text{ min.}^{[3]}$. This indicates there may be opportunity in NYS to reduce BTF vessel size or treat more gas with currently sized systems. The volumetric loading rate of H₂S into BTF at farms in NYS, however, is 0.18-0.20 lb./ft³/h, higher than rates typically reported for BTF removing H₂S, which range from 0.003-0.007 lb./ft³/h^[1]. While these systems are targeting odor not cleaning biogas, this large discrepancy indicate BTF vessels used by NYS farms are already scaled-down and may have trouble treating high concentration H₂S pulses. Thus, while smaller BTFs might save cost for treating average loading, a secondary treatment system (e.g. iron sponge) should be considered with these designs to ensure pulse loads are treated.

TRICKLING DENSITY

(Surface area standardized flow rate)

The trickling phase flow rate is set for a particular liquid-to-gas ratio, the minimum restricted by media desiccation, the maximum by biofilm dislodgement and tower flooding. Typically the ratio is set at $1.1-1.7\times$ the minimum (~20 gal./ft² cross sectional area/h), well below the trickling density of 120 gal./ft²/hr where biofilms can dislodge. While the water flow rate is typically fixed, increasing the trickling

density in counter-current BTFs can increase dissolved oxygen concentrations and is a potential strategy to improve the H₂S removal of high inlet loading events. High trickling densities can also increase BTF media liquid film thickness, limiting capture of emissions and increasing pressure drop^[4]. *As these tradeoffs suggest, there is the potential to optimize trickling density to improving oxygen delivery to SOB for increased sulfate production and reduced sulfur buildup*^[5].

CONTROL OF SULFUR-LADEN WATER DISCHARGE

The sulfur-laden water must be discharged at a rate that minimizes water usage but optimizes removal of accumulated breakdown products (i.e. sulfate, acids). In NYS, desulfurization BTFs which are operated under acidic conditions, typically discharge at a 2-hour time interval and not according to pH or conductance meters. There is opportunity to control these systems by meters instead of by time set points and discharge at a pH of 1.3 or a conductance of 14,000-21,000 µs/cm. Meters must be regularly calibrated to be accurate, and would be а required, but straightforward, maintenance if meters were used for control. If operators chose to rely on the use of time set points for flushing, the use of meters might not be necessary. Instead regularly scheduled spot measurements could be used to monitor system parameters.

OXYGEN DELIVERY

The oxygen $(O_2)/H_2S$ ratio is critical to BTF operation (see Part 2). To optimize the O_2 ratio in the BTF vessel, the air delivery rate could be controlled by a gas analyzer measuring inlet H_2S concentrations. A blower is typically used to mix air with biogas for O_2 delivery. Roughly one molecule of O_2 is needed for every molecule of H_2S for optimal treatment. As H_2S is ~80× more soluble in water than O_2 , large amounts of air are needed to deliver sufficient O_2 . To avoid biogas dilution with air, introduction of explosive levels of O_2 , and the formation of sulfur due to an O_2 limited environment, trickling water can be aerated to more effectively deliver dissolved O_2 to the biofilm. Venturi aeration systems have been used for this application^[6], and may be worth consideration.

INOCULATION, NUTRIENTS & PH BUFFERS

Most NYS farm biogas BTF operators inoculate systems at start-up. Few inoculate regularly during operation. Re-inoculations are likely unnecessary unless the BTF microbial community fails or is removed by cleaning. *To reduce lag following BTF cleaning, retaining trickling water to reinoculate cleaned media is recommended.*

The SOB community in BTF requires the addition of nutrients. There is opportunity to improve and cater nutrients to particular systems to optimize H_2S removal. Glucose for example, can be added to stimulate H_2S oxidation, but high doses can lead to

excessive microbial growth and pressure drop^[7]. Most BTF operators currently use a 8N - 8P - 6K - 0.1Zn - 0.02B - 0.02Mn - 0.01Cu - 0.02Fe nutrient solution. *There is likely opportunity to optimize nutrient additions, however, as to our knowledge there is a lack of research on the topic.*

Rapid pH drop can lead to a preferential generation of sulfur, while high pH results in the formation of products inhibitory to SOB activity^[5]. *Compounds can be added to the trickling phase to buffer pH (e.g. sodium hydroxide), extend their useful life^[1]*.

CLEANING

Regular (~15 min. every 2 hr.) flushes with jetted water and semi-annual (2× yr.) backwashing/bubbling and cleaning of BTF media are required to clean sulfur and prevent clogging. Capitalizing on the ability of SOBs to completely oxidize H₂S when oxygen is not limited, aeration and trickling can be run in the absence of biogas to stimulate SOB breakdown of sulfur deposits^[5]. This strategy may be useful during biogas-fueled, engine-generator set servicing and other downtimes to improve the efficacy of backwashing and reduce the frequency of manual cleaning.

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References

[1] Kennes C. & Viega M.C. (2013). Biotrickling filters. In: (Eds.) Kennes C., Veiga M.C. Air pollution prevention and control: Bioreactors and bioenergy. John Wiley & Sons. [2] Muñoz R, Meir L, Diaz I & Jeison D. (2015) A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Rev. Environ. Sci. Biotechnol.* 14: 727-759. [3] Montebello AM, Bezerra T, Rovira R, Rago L, Lafuente J, Gamisans X, Campoy S, Baeza M, & Gabriel D. (2013) Operational aspects, pH transition and microbial shifts of a H₂S desulfurizing biotrickling filter with random packing material. *Chemosphere* 93: 2675-2682. [4] Van der Hayden C., Demeyer P., Volcke E.I.P. (2015). Mitigating emissions from pig and poultry housing facilities through air scrubbers and biofilters: State-of-the-art and perspective. *Biosyst. Eng.* 134:74-93. [5] Fortuny M, Gamisans X., Deshusses M.A., Lafuente J., Casa C. & Gabriel D. (2011) Operational aspects of the desulfurization process of energy gases mimics in biotrickling filters. *Water Res.* 45:5665-5674. [6] Rodriguez G, Dorada A.D., Fortuny M., Gabriel D. & Gamisans X. (2014) Biotrickling filter for biogas sweetening: Oxygen transfer improvements for a reliable operation. *Process Safety Environ. Protect.* 92: 261-268. [7] Datta I, Fulthorpe R.R., Sharma S. & Allen D.G. (2007) High-temperature biotrickling filtration of hydrogen sulphide. *Appl.Microbiol. Biotechnol.* 74:708–16.

