4-1997

The Use of Wood Based Aerobic Bioreactor to Oxidize Hydrogen Sulfide

Wade C. Rayner
Western Michigan University

The Use of a Wood Based Aerobic Bioreactor to Oxidize Hydrogen Sulfide

by

Wade C. Rayner

A Thesis submitted
in partial fulfillment of
the course requirements for
the Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan

April 17, 1997

ABSTRACT

The central focus of this thesis was to study the possibility of and carry out an experiment dealing with biological oxidation of hydrogen sulfide. The biological reactor was to be a 5 inch in diameter, 14 inch tall PVC pipe filled with pine chips as a growth medium. The growth medium was to be seeded with thiobacillus thioxidans, a strain of sulfur-oxidizing bacteria. Hydrogen sulfide gas at approximately 50 parts per million was to be introduced into the reactor at a rate of 1.8 L/min, resulting in a retention time of approximately 60 seconds. Inlet and outlet gas samples were to be taken from the reactor every 20 minutes with subsequent H_2S analysis to be carried out by way of colorimetry. With an acclimation period to hydrogen sulfide of only 3 days for the bacteria, the experiment was expected to produce nearly complete hydrogen sulfide oxidation within the reactor once the experiment began. Unfortunately the acclimation period was closer to about 3 weeks and, due to poor scheduling, the reactor phase of the experiment was never run. Once acclimated, however, the bacteria did oxidize the hydrogen sulfide to apparent completion.

TABLE OF CONTENTS

INTRODUCTION

A number of issues came together to contribute to the idea that became this thesis. First of all, a number of conversations have come up in the last few years dealing with the distinct odor emanating from pulp mills utilizing the kraft chemical pulping process. Second was the growing interest in the environmental issues of this niche of the industry, ranging from the aesthetically disagreeable smell of kraft mills to the danger that these gases, particularly hydrogen sulfide, can pose if they are encountered in high enough doses. Naturally, a research project was born.

The focus of this thesis was to study the possibility of and carry out an experiment to oxidize hydrogen sulfide by way of an aerobic biological reactor. The growth medium for this experiment was to be pine wood chips, and the bacteria species was thiobacillus thioxidans, a strain of bacteria that lives and grows by digesting and oxidizing sulfur. The purpose of this study is to explore the possibility of oxidizing this and other total reduced sulfur gases, eliminate the odors caused by these gases, and hopefully present an alternative to Kraft mill gas treatment to eliminate odors emanating from these mills.

THEORETICAL AND BACKGROUND DISCUSSION

Once this thesis topic was decided upon, an extensive literature search had to be performed to find out if this had been done before, and if not then if it may be feasible. Several sources were located that dealt with the subject and they will be summarized below with respect to their relevance to this project.

First we will begin with the Kraft pulping process, the major producer of hydrogen sulfide (H_2S) in the pulp and paper industry. In the kraft liquor cycle the white liquor chemicals, sodium hydroxide (NaOH) and sodium sulfide (Na_2S), are introduced into a batch or continuous digester to "cook" wood chips. These active chemicals impregnate the chip and break down (solubilize) approximately 80% of the lignin, 50% of the hemicelluloses, and about 10% of the cellulose, essentially leaving the rest of the cellulosic material for further processing and papermaking. The remaining liquor that contains spent chemicals and solubilized lignin, hemicelluloses, and cellulose, called black liquor, is then concentrated through evaporation and chemical addition and incinerated in a recovery furnace. The remaining smelt is then dissolved in water and causticized to recover a portion of the original white liquor. The remaining white liquor is utilized in further cooking cycles (1).

Hydrogen sulfide is produced at several steps of the modern digestion and recovery processes. A significant amount of H_2S is released in digester blow and relief gases. Measurable amounts have been found in brown stock

washer vents immediately following chip digestion. The washed liquor then goes on to multiple effect evaporators where most of the moisture is evaporated off, carrying with it a substantial amount of H_2S. Remaining Na_2S in the black liquor is reduced to Na_2O and H_2S in the recovery boiler, where some, but not all, of the H_2S is then oxidized to form sulfide. Remaining H_2S is then released in the boiler exhaust gases. Small but measurable amounts are released at exhaust points further down in the recovery process (1).

Before we get on to possible treatment alternatives, we should know a little bit about H_2S. Hydrogen sulfide is one of four total reduced sulfur (TRS) gases found in the Kraft digestion and recovery processes. Others include methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, but hydrogen sulfide is the gas produced and emitted in the largest amounts (1). The approximate odor threshold, or the concentration that we start to smell it at, is at about 0.1 parts per million (ppm). Our odor threshold limit, or the amount above which we cannot smell it any longer, is 10 ppm. Serious eye injury can begin at concentrations of about 50 ppm, with immediate collapse from respiratory paralysis occurring at 1000 ppm (2). Death from H_2S exposure is possible, but rare. As long as a mill is utilizing the kraft process, H_2S is being emitted, and the wind is blowing, the characteristic rotten egg odor associated with H_2S can be noticed up to several miles from the mill.

A number of articles and research papers have been published that deal with H_2S treatment, and many of them utilize biological processes. A research project taken up by the environmental engineering program at USC

dealt with air pollution control measures needed at publicly owned treatment works (POTWs). Bench and pilot scale biofiltration reactors were set up to control low and variable amounts of VOCs and H_2S produced at these wastewater treatment facilities. Granular activated carbon (GAC) and yard waste compost were utilized as biofilter media. The cylindrical bench-scale reactors measured 7.5 cm in diameter and 150 cm in length. The biofilter media filled approximately 100 cm of the reactor length. Flow rates through the reactor ranged from 0.7 to 2.8 m^3/min, resulting in retention times from 70 to 17 seconds. Activated sludge was added to all reactors to provide seed bacteria, while a suspension of bugs from a sulfide rich corrosive environment, including some identified as thiobacillus thioxidans, were added to the low pH controlled GAC reactor. This low pH reactor was controlled at pH 2. Inlet air streams into the reactors contained from 1 to 10 ppm of H_2S throughout the experiment. The experiment was carried out from August of 1993 through January of 1995. Continuous sampling over that time revealed that H_2S removal was nearly complete (95-100%), and that those types of reactors could be feasible for odor reduction at an H_2S concentration of about 1 to 10 ppm (3).

Another research project taken up by the University of Florida focused on the design and operating principles of H_2S biofiltration. They set up a similar biofilter system made up of yard waste composts. H_2S concentrations, residence times in the reactors, and reactor temperature and moisture content were varied throughout the experiment. Results of the

experiment showed that H_2S could be removed with 99% efficiency at a concentration of up to 2650 ppm, the maximum concentration analyzed in the study. They found that to maintain this efficiency, they needed to gauge the inlet velocity to the H_2S concentration to ensure sulfide diffusion into the liquid phase, that the moisture content in the biofilter needed to be at least 30 percent, and that maximum efficiency occurred at bed temperatures of 25 to 50 degrees Celsius. Efficiency decreased rapidly below 20 C, and decreased gradually when over 50 C. They also found that a minimum retention time of about 20 seconds was required so that the H_2S gas could diffuse into the liquid phase where the bugs could attack it. Sulfuric acid was the primary product of H_2S biological oxidation and removal efficiency of H_2S was maximized at pH values between 3 and 8 (4).

Several examples of industrial applications were also investigated. All of those found dealt with H_2S production at wastewater treatment plants in the southern U. S. A set of 7 foot diameter mobile-bed packed scrubber columns were installed at a reverse osmosis water treatment plant in Jupiter, Florida to oxidize H_2S produced by reduced sulfides in the wastewater supply. These scrubbers, which stand about 30 feet tall, handle air at up to 15,000 scfm and have kept outlet concentrations of H_2S under the guaranteed limit of 4 ppm since they began running. They are said to be running at 98% efficiency as of June of 1992 (5).

A full scale biofilter was installed by the Hillsborough County (Fla.) Public Utilities Department and was tested as a lower cost and more highly

efficient alternative to other H_2S elimination methods such as packed tower scrubbers, carbon columns, and mist scrubbers. Two highly organic compost-like substrates were used, and the reactor was evaluated over a years time. After a 14 day period of bacteria acclimation, the bioreactor successfully reduced H_2S emissions from the plant from 85 to 0 ppm over the entire time of the evaluation. Retention times were as low as 30 seconds and media leachate pH was recorded as low as 0.9 without any decrease in H_2S removal efficiency (6).

Analysis of this literature revealed that biological oxidation of H_2S is possible and practical, and that further study can work to support these findings and expand biological treatment of H_2S to the pulp and paper industry. It was my hope that the results of this experiment would do just that.

EXPERIMENTAL

The reactor for this experiment was to be 5 inches in diameter and 14 inches in length, with approximately 12 inches of that length filled with moist pine wood chips. The chips were to be seeded with a culture of thiobacillus thioxidans acclimated to H_2S and H_2S has was to be blown through the reactor at approximately 1800 mL/min, resulting in a retention time of approximately 60 seconds. A 50 gallon polyethylene bag filled with air at approximately 50 ppm H_2S was to be the supply for the reactor, so that the experiment would run for approximately 3 hours. Samples were to be taken from the bottom and top air pockets in the reactor (inlet and outlet, respectively) every 20 minutes and tested for H_2S content by way of colorimetry (see Appendix I). Kitagawa sampling tubes were to be used in calibrating the colorimetric curve.

In order for the experiment to run in the allotted time, the thiobacillus culture would need to be acclimated to H_2S gas before experimentation could commence. The Thiobacillus culture was purchased from the American Type Culture Collection in January of 1997, and the required salt solution (Appendix II) was made up in March. One hundred milliliters of this solution was retained in a 200 mL small mouth sidearm flask and 1 mL of the pure culture was added to it. A rubber stopper with a Pyrex tube was used to seal the mouth of the flask, and H_2S has at about 50 ppm was bubbled through the solution. A faint turbidity in this solution after 2 to 3 days time was to indicate

bacterial acclimation and growth, but this did not happen after a full week of bubbling. Precipitated sulfur granules were added to the solution in an attempt to stimulate growth, but it did not appear to help. Another salt solution was made up (in the same setup as before) and the H_2S gas stream was then split between the two flasks and run for 2 more weeks. A faint turbidity finally became apparent in the second flask during the second week of April. The two flasks and the original pure culture were then Gram Stained (see Appendix III) and examined under a 100* magnification microscope to see if the bacteria were finally growing. There was no sign of the bacteria in the original salt solution, but they did show up in the pure culture and in the second salt solution.

At this point we readministered the second, successful salt solution to the H_2S injection as before. After another day of H_2S injection, we tested the inlet air to the solution for H_2S and the outlet air immediately after bubbling. These tests were carried out with Kitagawa sampling tubes. We decided to halt the experiment at this point to give time for preparation of this report and the subsequent presentation before the WMU College of Engineering and Applied Sciences on April 17th.

RESULTS

Due to the untimely end of this experiment, there is not a great deal of data to present. What there was is as follows.

Gram Stain results:

Pure culture: positive ID.

1st acclimation attempt: negative ID.

2nd acclimation attempt: positive ID.

Artists rendering of thiobacillus thioxidans under 100* magnification:

Kitagawa sampling results:

Inlet port H_2S concentration: 50 ppm.

Outlet port H_2S concentration: 0 ppm.

DISCUSSION OF RESULTS

The positive identification in the second salt solution flask confirmed my belief that I could grow the bugs in this type of experimental setup. Unfortunately, the critical error in this experiment was the lack of accurate timing. Personal communication with the biochemistry department at WMU led me to believe that the bacteria would acclimate to the H_2S in about a weekends time (7). Unfortunately, I followed this suggestion instead of the two to three weeks suggested by the literature (6). As a result I did not allow enough time to fully carry out the experiment.

The quick testing with the Kitagawa tubes indicated more favorable results. After nearly two weeks of no apparent growth in the inoculated solutions, we were afraid that maybe the H_2S concentration bubbling into them may not have been as high as had been previously calculated. Ten milliliters of pure H_2S had been injected into the polyethylene bag as it was filled with air, resulting in a final bagged concentration of about 52 ppm. The Kitagawa sample indicated a concentration of approximately 50 ppm, showing that most, if not all, of the gas was being transferred directly to the salt solution at the set rate of 20 ml/min. The exit Kitagawa tube analysis of 0 ppm indicated that all, or at least all but an insignificant amount, of the H_2S was diffusing into the water for bacterial consumption. This was what we had hoped for and what we believed would happen.

If we had given ourselves more time to complete the actual experiment with the wood chip reactor, then more data would have been available.

CONCLUSIONS

Based on what little data that was collected, it can be concluded that that thiobacillus bacteria were readily adaptable to H_2S and that a feed rate of 20 ml/min of gas at 50 ppm H_2S was sufficient to stimulate and maintain growth.

If the expected experimental work would have been completed on time, then there probably be more definitive conclusions. I suspect that with a sufficient moisture concentration in the reactor and a heat source to keep the reactor temperature above 20 degrees Celsius, then the bacteria would probably have oxidized the polluted gas as planned.

RECOMMENDATIONS

The primary recommendation for further work is to complete the experiment that was started. It finally started to show promise near the end, but time unfortunately ran out. Future researchers may find that the thiobacillus culture may not react well with the highly organic pine chips, and if that happens then a similar experiment can probably be attempted with more adaptable bacteria commonly found in composting materials. Thiobacillus bacteria work well in low pH environments, but other variables can lead to their demise (2). These other bugs can probable be located for a cheaper price than the thiobacillus cultures.

If this proves to work well in future experiments, then further study could concentrate on setting up a trial - size reactor connected to off-gases from the various kraft exhaust systems. I truly believe that with the proper setup, connections to exhaust ports from point sources in the mill, and routine maintenance that a biofilter or bioreactor setup could save kraft mills from the offensive odor associated with H_2S and the money spent on older, less efficient, and more expensive pollution control equipment.

WORKS CITED

1. *Smook, G. A.*, "Handbook for Pulp and Paper Technologists," second edition, Angus Wilde Publications, Bellingham, WA, 1992.

2. "Hydrogen Sulfide," Committee on Medical and Biologic Effects of Environmental Pollutants, National Research Council, University Park Press, Baltimore, MD, 1979.

3. *Devinny & Webster*, "Biofiltration of Odors, Toxics and Volatile Organic Compounds from Publicly Owned Treatment Works," Environmental Progress, Vol. 15, no. 3, p. 141 - 147.

4. *Yang & Allen*, "Biofiltration Control of Hydrogen Sulfide - 1. Design and Operational Parameters," Air and Waste, Vol. 44, July 1994, p. 863 - 868.

5. "H_2S Oxidation Process Solves Odor Problems," WATER/ Engineering and Management, June 1992.

6. *LeBeau & Milligan*, "'Homemade' Biofilter Controls Hydrogen Sulfide Odors," Water Environment and Technology, March 1994, p. 15-18.

7. *Eisenberg, Dr.*, Western Michigan University Department of Biochemistry, personal communication throughout this project (10/96 - 4/97).

8. *Howell & Boltz*, "Colorimetric Determination of Nonmetals," Second edition, John Wiley and Sons, Inc, New York, 1978.

9. ATTC, Culture Medium 125, Thiobacillus Medium preparation instructions.

10. *Eisenberg, Dr.*, WMU Microbiology lab gram staining instructions.

APPENDICES

APPENDIX I

Colorimetric Determination of Hydrogen Sulfide in Gases by the Methylene Blue Method (8).

Reagents

Stock Zinc Acetate Solution (20%): Dissolve 200 g. zinc acetate in 1 liter distilled water.

Dilute Zinc Acetate Solution (2%): Dilute 100 mL of the stock solution to 1 liter with distilled water and acidity with bout three drops acetic acid.

Diamine Reagent: Dissolve 0.15 g *p*-amino-N,N-dimethylaniline sulfate in a cooled mixture of 100 ml concentrated sulfuric acid and 50 ml distilled water.

Ferric Chloride Solution: Dissolve 2.7 g $FeCl_3$ $6H_2O$ in 50 ml concentrated hydrochloric acid and dilute to 100 ml with distilled water.

Procedure

Bubble the gas sample into 50 ml of the 2% zinc acetate solution contained in a wide-mouthed bottle until a faint turbidity forms, measuring the volume of gas used. Wash the contents of the bubbling bottle into a 1-liter volumetric flask with the 2% zinc acetate solution, rinsing out the bottle carefully, adjust the volume to 1000 ml with the 2% zinc acetate solution, and mix. Pipet 50 ml of this solution into a beaker or flask and cool to at least 10 C in an ice-water bath. Add 5.0 ml of the diamine reagent, stir and add 1.0 ml of the ferric chloride solution. Stir and measure the color with the spectrometer-20 colorimeter after standing 15-30 minutes. Prepare a blank similarly with all reagents and use it to zero the instrument. Prepare several samples of known concentrations to calibrate the instrument (8).

APPENDIX II
Thiobacillus Medium Salt Solution

Reagents

$(NH_4)_2SO_4$, 0.2 g.
$MgSO_4$ $7H_2O$, 0.5 g.
$CaCl_2$, 0.25 g.
KH_2PO_4, 3.0 g.
$FeSO_4$, 5.0 mg.
Tap water, 1.0 L

Procedure

Prepare the salt solution, including all reagents listed above, in a 1 liter flask until all reagents dissolve. Pour 100 ml of salt solution into a 200 ml sidearm flask, add 1.0 ml of pure culture, and bubble H_2S gas through the medium until a faint turbidity forms (7, 9).

APPENDIXIII
Microscopic Analysis of Thiobacillus

Materials

Pure Thiobacillus culture to be examined.
H_2S adapted Thiobacillus culture.
H_2S adapted Thiobacillus culture containing sulfur granules.
Microscope slides.
Gram staining solutions:
Hucker's Crystal violet.
Gram's Iodine.
95% Ethyl alcohol.
0.25 % Safranin.

Procedure

A. Prepare and heat-fix thin smears of each thiobacillus culture.
B. Stain the slides as follows:
1. Flood the crystal violet for one minute.
2. pour off excess dye and wash gently in tap water and drain the slide against a paper towel.
3. Flood the smears with Gram's iodine for one minute.
4. Wash with tap water and drain carefully (Do not blot).
5. Wash with 95% alcohol for 15-20 seconds or drip onto slide held at slight angle until blue color stops coming out of smear.
6. Wash with tap water at the end of the 30 seconds to stop the decolorization. Drain.
7. Counterstain with 0.25% safranin for 30 seconds.
8. Wash, drain, blot, and examine under oil at 100 * magnification (10).