Spring 12-5-2014

Pyrolysis of Human Feces: Odor and Odor Treatment Options

Elizabeth A. Travis
University of Colorado at Boulder, zeetravis@gmail.com

PYROLYSIS OF HUMAN FECES: ODOR AND ODOR TREATMENT OPTIONS

By

ELIZABETH (ZEE) TRAVIS

B.S., University of Colorado, 2009

A thesis submitted to the Faculty of the Graduate School of the
University of Colorado at Boulder
in partial fulfillment of the requirement for the degree of
Master of Science
Department of Civil, Environmental, and Architectural Engineering
2014

This thesis entitled:

Pyrolysis of Human Feces: Odor and Odor Treatment Options

Written by Elizabeth Ann Travis

has been approved for the

Department of Civil, Environmental, and Architectural Engineering

_____

Dr. Karl G, Linden

_____

Dr. JoAnn Silverstein

Date: December 5, 2014

The final copy of this thesis has been examined by the signatories, and we
Find that both the content and the form meet acceptable presentation standards
Of scholarly work in the above mentioned discipline

Travis, Elizabeth Ann (M.S. Civil Engineering, Department of Civil, Environmental, and Architectural Engineering)

Pyrolysis of Human Feces: Odor and Odor Treatment Options

Thesis directed by Professor Karl G. Linden

Abstract

In response to the Reinvent the Toilet Challenge, the University of Colorado Boulder developed a toilet technology – the Sol-Char toilet – that uses concentrated sunlight and flexible fiber-optic cables to pyrolyze human feces, rendering human waste safe and transforming it into a usable char. However, the release of large amounts of volatile sulfur compounds as well as exhaust gases represents a crucial challenge associated with toilet operation. The objective of this research was to quantify the odor and hydrogen sulfide released during the pyrolysis of human feces and to explore treatment options. It was found that the pyrolysis of between 160-900 grams of feces released hydrogen sulfide peaks between 25 and 90 ppm. An odor detection threshold of 510,000 odor units per cubic foot was determined. The ramp rate and pyrolysis temperatures were varied during these experiments to learn how this influenced the quantity and timing of hydrogen sulfide release. To test the effectiveness of adsorption onto feces-derived chars for the treatment of hydrogen sulfide, the hydrogen sulfide breakthrough capacity of three chars created at various temperatures was investigated. The chars evaluated were 300°C, 450°C, and 900°C fecal char, 300°C and 1200°C pine char, and 900°C bamboo char. Breakthrough experiments indicated that 900°C fecal char had the highest hydrogen sulfide breakthrough capacity. Analysis of char surface characteristics was performed using FTIR, SEM/EDS, BET analysis, and pH measurements in order to understand the mechanism of hydrogen sulfide adsorption for each char. The feasibility of biofiltration for exhaust treatment was also investigated. Preliminary tests using a pilot scale

biofilter indicate that biofiltration represents a potential mechanism for the treatment of the complex gas mixture associated with fecal pyrolysis exhaust.

Acknowledgements

I would like to thank my advisor, Dr. Karl Linden, and my committee members, Lupita Montoya and JoAnn Silverstein, for their support and encouragement throughout the process of working on this project. In addition, Dr. Tesfa Yacob has gone above and beyond as a mentor and colleague, helping me with the planning, execution, and analysis of my research all the way through. Thanks to Dr. Scott Summers, Dr. Rita Klees and everyone on the Sol-Char team who provided wisdom and support. A special thanks to BJ Ward, Lauren Hafford, and Ryan Mahoney for sharing their unsurpassed knowledge as engineers and fecal char experts, as well for providing timely encouragement and advice. Without the perseverance of BJ and Lauren, the materials necessary to complete this research may not have been obtained. Thanks to Dana Hauschutz for solving the many electrical issues that arose throughout the project. Thanks to the Linden lab, and especially James Rosenblum, for sharing space and providing guidance. Thanks to the Ryan lab and Jess Dehart for allowing me to use their chemical hood. Thanks to the Noble lab for the use of their FTIR machine and William McDanel for training me on its use. Thanks to the Ren Lab for sharing their space and Tyler Huggins for performing SEM-EDS analysis on the char samples. Thanks to the Hernandez lab for the use of their hydrogen sulfide monitor. Thanks to Jeanette Neethling and Choolwe Mandona and all of the students and staff in the sustainability wing for their endless optimism and patience in discussing all things RTT. Thanks to Gayle Van Durme at Black & Veatch for his advice regarding appropriate odor treatment technology for the developing world. Thank you to all of my friends and family for their love and support throughout graduate school. Finally, thanks to the Bill and Melinda Gates Foundation for providing the funding that made this project possible.

Table of Contents

List of Tables

List of Figures

List of Equations

1. Introduction & Thesis Outline

1.1. The Sanitation Challenge & Reinventing the Toilet

1.1.1. Sanitation Coverage

Few things have done more to improve human health than sanitation. The introduction of toilets, sewers, and wastewater treatment systems was responsible for a rapid decline in infectious disease in the middle of the 19th century. Despite the accepted relationship between sanitation and health, a staggering 2.5 billion people globally lack access to improved sanitation [1]. These people are at high risk for exposure to diarrheal disease and microbial infections, leading to huge consequences for their health and economic status. Ultimately, lack of sanitation coverage contributes to more than 1.8 million deaths associated with diarrhea every year [1]. One of the reasons for this discrepancy is a lack of demand. The alternatives currently available in developing countries are less expensive and are not resource intensive, but can be unattractive options for numerous reasons including unworkable designs, odors, insects, lack of infrastructure, and aesthetics [2]. However, the flush toilet and waste infrastructure entrenched in the developed world requires excessive amounts of land, energy, and water. Global challenges such as rapid urbanization, informal settlement, water scarcity, and pollution are emerging issues that make the flush toilet and sewage infrastructure financially and physically infeasible on a global scale. Current leaders in sanitation aim to transform the toilet into a status symbol, integrate the toilet into local economies, and collaborate with other sectors to distribute and maintain toilets [3].

1.1.2. The Bill & Melinda Gates Reinvent the Toilet Challenge

The Bill and Melinda Gates Foundation (BMGF) aims to enhance global sanitation coverage by investing in innovative and affordable new technologies. Through their Reinvent the Toilet Challenge they have funded the development of a waterless, hygienic, stand-alone toilet that

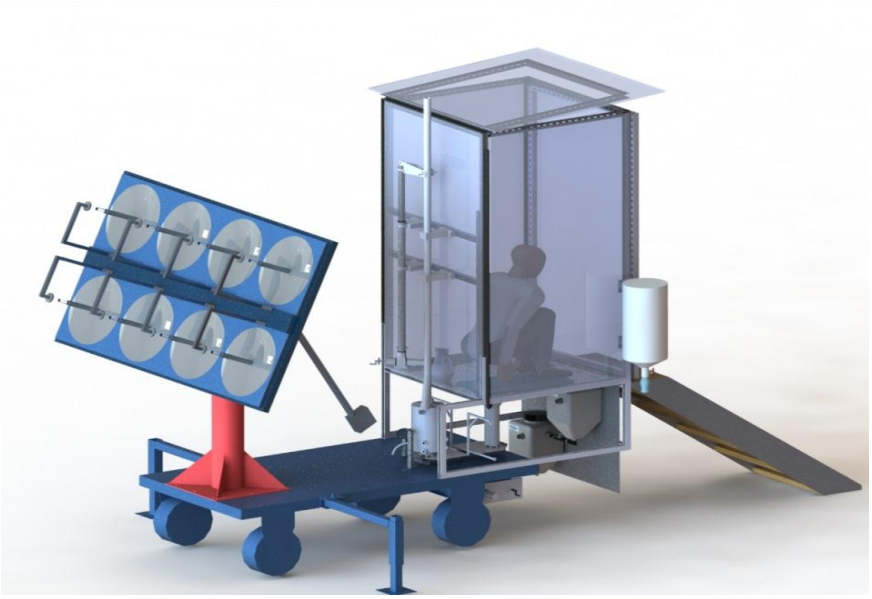
functions without a connection to water or electricity [2]. Many of the technologies the BMGF is exploring are predicated on the idea of heating or combusting human waste.

1.2. Sol-Char Sanitation

1.2.1. Technology Overview

As part of the Bill & Melinda Gates Reinvent the Toilet Challenge, the University of Colorado designed the Sol-Char Toilet, shown in **Figure 1**. It uses concentrated solar energy

Figure 1- Sol-Char Toilet



and flexible fiber optic cables to pyrolyze human waste. The reaction process renders feces pathogen free and transforms it into a mixture of biochar and pyrolysis gas, reducing the waste volume by up to 90%. The ratio of biochar to pyrolysis gas generated can be controlled by varying the pyrolysis reactor conditions. Biochar has the potential to increase the ability of soils to retain water and macronutrients and release them slowly [4]. It also contains many of the micronutrients required by plants [5], and is safer than commonly used fertilizers such as manure, as it

is disinfected at high temperatures. The viability of fecal biochar as an agricultural amendment, an adsorbent, and a solid fuel has been established throughout the process of designing the Sol-Char toilet.

1.2.2. Odor & Exhaust Challenge

One of the largest challenges associated with the Sol-Char Toilet is treatment of the exhaust released during fecal pyrolysis. The exhaust stream is malodorous and contains gases that are a health and human safety concern at high concentrations. In order to ensure that the Sol-Char toilet is attractive to users and does not pose a threat to human health and safety, the pyrolysis exhaust stream must be treated.

While few studies have focused on the odors directly from feces, information on odors from wastewater treatment plants provides an important starting point. In a study looking at what contaminants exist in sewer off gas, carbon dioxide, volatile oils, hydrogen sulfide, methyl mercaptans and ethyl mercaptans were found [6]. Of these, hydrogen sulfide has the overall lowest odor detection threshold [7], and is also extremely dangerous at high levels. For this reason, it is a good surrogate for odor measurement and removal.

This study first quantified and then identified and explored treatment options for the odor and exhaust produced during the fecal pyrolysis process. Based on literature, selection of hydrogen sulfide as the primary removal target, and the BMGF's criteria for a stand-alone toilet, adsorption and biofiltration were chosen as the best candidates for odor control and treatment of fecal pyrolysis exhaust. This research characterized the usefulness of both fecally derived and wood based chars for adsorption of hydrogen sulfide, while biofiltration was assessed for its ability to treat the complex exhaust emitted during fecal pyrolysis as a whole.

1.3. Thesis Outline

This thesis is separated into chapters based on the three main research objectives of the project: to characterize the hydrogen sulfide content and odor associated with fecal pyrolysis exhaust; to remove hydrogen sulfide from the exhaust, and to treat the exhaust as a whole for odor and other exhaust components. Chapter 2 provides background information on the pyrolysis process, char and its potential uses, the expectation for the composition of fecal pyrolysis exhaust, and information on all prospective odor and exhaust treatment options. Following this background information, the next three chapters address the main research objectives. Chapter 3 focuses on characterizing the release of hydrogen sulfide and odor during fecal pyrolysis, chapter 4 explores the effectiveness of feces-derived char, pine char, and bamboo char for the adsorption of hydrogen sulfide, and chapter 5 looks at the feasibility of using biofiltration to treat the odor and complex gas mixture associated with fecal pyrolysis exhaust. In order to demonstrate the implications of the results, the potential of scaling up adsorption and biofiltration treatment systems for the treatment of fecal pyrolysis exhaust is examined in chapter 6. Finally, chapter 7 brings together the conclusions discussed in previous chapters and discusses further research that would supplement this thesis.

2. Background

2.1. Pyrolysis & Char

2.1.1. The Pyrolysis Process and Char Characteristics

Pyrolysis is the thermal decomposition of organic matter at high temperature and low oxygen conditions into a carbonized deposit of organic compounds. Pyrolysis gas typically contains CO_2, CO, CH_4, H_2, C_2H_6, and C_2H_4. Exhaust from fecal pyrolysis has these gases as well as malodorous sulfur compounds [8].

The characteristics of the char produced via pyrolysis are dependent on a number of essential factors. The two most important are feedstock properties and pyrolysis temperature. Both of these will affect the bulk density, surface area, pore structure and surface chemistry. These in turn have a huge impact on the chars reactivity and thus functionality. In general, for wood and cellulosic biomass, as pyrolysis temperature increases, the internal surface area and distribution of micropores increase. This makes high temperature chars a competitive adsorbent for water and air pollutants. As temperatures increase, the percent ash and percent elemental carbon increase, while the percent hydrogen and oxygen in char decreases [9]. In addition, more species volatilize at higher temperatures. The increased conversion to gas ultimately leads to lower mass yields of biochar [10, 11]. Feedstocks like manure have a higher initial mineral and inorganic content than agricultural feedstocks. This results in chars that have higher relative ash content and lower relative carbon content [10].

2.1.2. Char Uses

Depending on the specific characteristics of each char, there are a number of advantageous uses. These include use as a soil amendment, an adsorbent for water and air treatment, and as a fuel and replacement for charcoal. Biochar can increase soil fertility by improving water quality, reducing nutrient leaching, and reducing soil acidity [12]. Increasingly, biochar is being looked at

as a low cost, lower energy alternative to activated carbon in the field of pollution mitigation for both air and water contaminants. Studies at the University of Colorado as part of the Reinvent the Toilet challenge have found that low temperature fecal chars bound into briquettes using molasses and lime had a strength and energy content that was comparable to commercial charcoal briquettes [13]. In addition, soil carbon sequestration through biomass pyrolysis is a proven means of mitigating greenhouse gases [14]. In the natural carbon cycle, plants absorb CO_2 as they grow and quickly return it the atmosphere when they die and decompose. When they are instead subjected to pyrolysis, the result is charcoal, which in its elemental form is difficult to process and does not decay very fast. Lastly, though the mechanism is unknown, soil containing biochar also releases less methane and less nitrous oxide than its untreated counterparts [15].

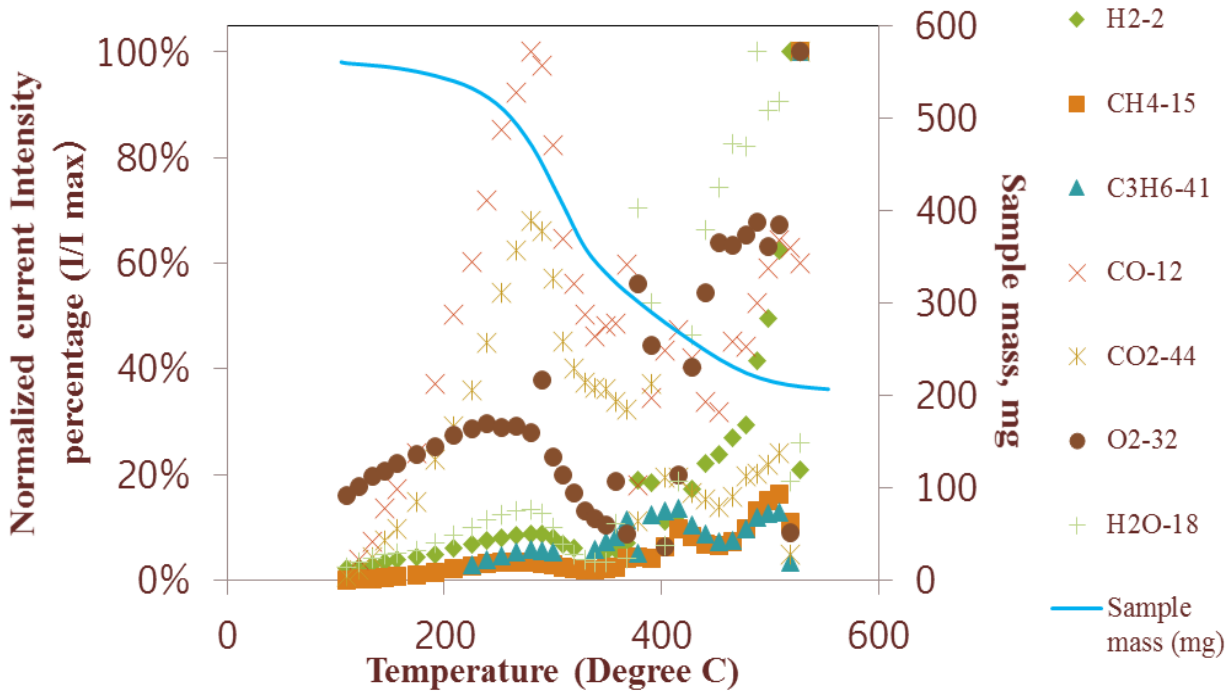
2.2. Fecal Pyrolysis Exhaust Characterization

2.2.1. Fecal Exhaust Gas components

Thermo gravimetric analysis was undertaken by the Sol-Char research team in order to verify the gas composition of fecal pyrolysis exhaust. Results confirmed the presence of combustible gases, including carbon monoxide, hydrogen, and methane and are shown in

Figure 2. The analysis correlates with what is expected from the chemical decomposition of organic materials in the absence of oxygen [8]. The tests was performed on 3.2 grams of waste heated at a 10K/minute ramp rate to 105°C, held for 2 hours, and then heated up to 550° at the same rate.

Figure 2- Thermo gravimetric analysis to detect pyrolysis gases from Yacob et al. [16]



2.3. Odor & Sanitation

Odor must be dealt with in order to make a waterless, hygienic, stand-alone toilet feasible. The odor challenge becomes particularly problematic when working outside conventional sanitation options. The BMGF is working towards innovative sanitation solutions, and standard methods of dealing with odor must be re-explored to understand their feasibility within this new framework. Dry sanitation methods mean that water is no longer used to dilute and displace fecal odor. Dilution, the most commonly used method for treating the odor associated with current dry sanitation technologies in developing countries, does not always work and in some cases has made

the use of toilets less attractive. In most dry sanitation cases, but especially in the case of the Sol-Char toilet, a more rigorous mechanism for treating fecal odor is necessary. Any combustion or heat based waste treatment technology would require a technology that treats the exhaust stream for a high concentration of hydrogen sulfide and excessive odor as a result of the accelerated release of odor causing compounds in feces and the general odor associated with combustion.

2.3.1. Odor Causing Exhaust Compounds

A literature review was performed to generate a list of the compounds responsible for fecal odor. The compounds found to be most important are volatile sulfur compounds, such as hydrogen sulfide, methyl sulfide, methanethiol, dimethyl disulfide, and dimethyl trisulfide, and also the organic compounds of skatole, and indole [6]. The strong odor rotten egg odor emitted by feces is attributed to the sulfur volatiles hydrogen sulfide, methanethiol, and dimethyl sulfide [17]. Because the Sol-Char system functions by accelerating drying, the concentrations of these odor causing compounds are expected to be higher in this system than in systems where the breakdown of waste is not hastened.

Hydrogen sulfide is commonly identified as the dominant nuisance odor associated with feces [18] and is also extremely toxic and corrosive. Consequently, it was used to direct a literature review of odor control methods for fecal pyrolysis exhaust.

2.3.2. Hydrogen Sulfide

H_2S is a colorless, combustible and toxic gas. It is found naturally and produced through anthropogenic processes. One common mode of production in nature is the reduction of sulfates or sulfur containing organic compounds by anaerobic bacteria and it is found naturally in many places including natural gas, crude petroleum, and hot springs. In feces, volatile sulfur compounds are largely the result of the metabolism of sulfhydryl-containing amino acids by gut bacteria [19]. Hydrogen sulfide is also a byproduct from wastewater treatment, manufacturing, and the

purification of natural and refinery gases. Since H_2S is approximately 20% heavier than air it tends to accumulate in depressions below its release point, increasing the risk that this gas will reach dangerous concentrating in low areas. Hydrogen sulfide must be dealt with not only as an odor problem, but also as a health risk for potential toilet users. **Table 1** below provides the health and safety impacts of hydrogen sulfide as a function of concentration. Corrosion is another issue associated with hydrogen sulfide itself as well as with sulfate, the oxidized form of sulfur [20]. This must also be considered when designing an odor control module.

Table 1- Health consequences associated with various hydrogen sulfide concentrations taken from the Occupational Health and Safety Administration [21]

Concentration (ppm)	Symptoms
0.00011-0.00033	Typical background concentrations
0.0005-1.5	Odor threshold when the rotten egg smell is first noticeable
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep; Airway problems in some asthma patients; Odor becomes more offensive between 3-5 ppm
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
30	Above 30 ppm, the odor can be described as sweet or sickeningly sweet
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour; May cause digestive upset and loss of appetite
100	Coughing, eye irritation, olfactory fatigue after 2-15 minutes; Altered breathing, drowsiness after 15-30 minutes; Throat irritation after 1 hour; Gradual increase in severity of symptoms over several hours; Death may occur after 48 hours
100-150	Olfactory fatigue or paralysis
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour; Pulmonary edema may occur from prolonged exposure
500-700	Collapse within 5 minutes; serious damage to the eyes in 30 minutes; death between 30-60 minutes
700-1000	Loss of consciousness within 1-2 breaths; breathing stops; death occurs within minutes.

1000-2000	Death

Hydrogen sulfide is a weak acid with dissociation constant, pKa_1, of 7.04. Its solubility in water at 20 ºC is 1 g in 242 ml. However, temperature and pH affect the solubility of H_2S. In general, low pH and high temperature favor evaporation [19]. Warm, damp environments favor the oxidation of hydrogen sulfide to sulfate and its ionization to the sulfhydryl anion (SH^-) is increasingly favored as pH rises. **Table 2** lists the physio-chemical properties of hydrogen sulfide.

Table 2- Properties of Hydrogen Sulfide taken from the U.S. EPA [22]

Molecular Weight	34.08 g
Vapor Pressure	15,000 mm Hg at 25 ºC
Density	1.5392 g/L at 0 ºC, 760 mm Hg
Boiling Point	-60.33 C
Water Solubility	3980 mg/L at 20 ºC
Dissociation Constants	pKa_1 = 7.04; pKa_2=11.96
Conversion Factor	1ppm = 1.39 mg/m^3

Exposure to high concentrations of hydrogen sulfide represents a very serious human health threat and should be avoided at all costs. The consequences of medium and long-term exposure to a low concentration of hydrogen sulfide affect human health has not been characterized. Thus, keeping exposure to a minimum is the best course of action. Based on the concentration data in **Table 1**, the goal of this project was to prevent hydrogen sulfide exposure above 1 ppm. Treating gas to 1 ppm or lower ensures that air released into the environment will

be diluted sufficiently by ambient air to prevent dangerous concentrations or unpleasant odors in the immediate environment.

2.3.3. Odor Quantification

Olfactometers are used to gauge the odor detection threshold of substances. To quantify odor intensity, olfactometers introduce an odorous gas as a reference point against which other odors are compared. This standard gas can be used to gauge individual odor sensitivities. The newest olfactometers, dynamic dilution olfactometers, use a panel of individuals whose sensitivity has been confirmed to rest within an appropriate range to define odor concentrations and thresholds [23]. A constant flow of pressurized pure air is continuously run past a panelist's nose. The odor compound is then introduced into this airstream and the dilution factor is decreased until an odor change is detected [23]. For this research odor was quantified using odor units per cubic meter of air (OU/m^3). The perception or detection threshold of an odorous gas can be defined as the gas concentration at which 50% of a human odor panel perceives the presence of an odor. The perception threshold is equivalent to 1 OU/m^3 and the number of dilutions of the odorant mixture required to reach this threshold is used to define the concentration of odor units of a particular odorous gas. To our knowledge, no published work exists that quantifies the odor associated with fecal pyrolysis gas.

2.4. Odor Treatment Techniques

There are a number of methods commonly used to treat odor in industry. The strengths and weaknesses associated with each in the context of treating fecal pyrolysis exhaust are discussed below.

2.4.1. Thermal & Catalytic Oxidation

Thermal Oxidation

The only effective exhaust treatment system which does not require the use of sorbents or catalysts is a thermal oxidation approach. Thermal oxidation has been shown to be very effective for the treatment of a broad range of chemical contaminants found in the Sol-Char exhaust, including H_2S and CO. Contaminated air must be heated to temperatures as high as 500-800°C for 1 second or more [24]. However, an efficient heat recovery system can be used to lower activation energy requirements. This is a promising technology for exhaust treatment. However, the current Sol-Char prototype does not have the capacity to reach temperatures high enough to effectively treat all of the compounds that are part of the matrix of fecal pyrolysis exhaust. This method also requires a high energy input. It would be an interesting option to explore as the technology associated with pyrolysis advances if money and resource availability were less of a restriction on the toilet design.

Catalytic Oxidation

Catalytic oxidation is a form of thermal oxidation that depends on a solid heterogeneous catalyst in order to lower oxidation temperatures. This approach would be effective against the carbon monoxide found in the exhaust. However, with a complex mixture like the exhaust from the Sol-Char toilet, rapid fouling of any catalyst is expected, making this method an ineffective long term solution for a stand-alone toilet [25]. Having a catalyst that requires continual replacement is both logistically and financially infeasible.

Claus Process

The current industry standard for hydrogen sulfide treatment is the Claus Process. This process involves both a thermal and catalytic step to transform gaseous hydrogen sulfide into liquid sulfur [26]. However, the relatively low concentration of sulfur associated with the pyrolysis

exhaust and the high energy demand associated with this process make it unsuitable for a small scale reproduction.

2.4.2. Wet Scrubbing

Use of pure water for scrubbing is limited to pollutants with high water solubility, ex. SO_2. One of the primary targets for effective odor treatment, H_2S, requires the use of challenging liquids such as concentrated caustic solutions [27]. The dangers associated with handling these liquids and the complications concomitant with transporting them make this process an unrealistic option for treating the odor associated with fecal pyrolysis gas.

2.4.3. Adsorption

Adsorption is an effective treatment for most gases, but the appropriate sorbent material will vary depending on the gas to be treated. There are two types of adsorption: physical and chemical. Physical adsorption is the result of week van der waals forces, has low binding energy, and is reversible. Chemical adsorption involves a reaction between the adsorbent and the adsorbate, generates a new bond, is very specific, has a high binding energy, and is difficult to reverse [28]. Sorbent regeneration is possible with selected pollutants and simple mixtures such as organic solvents in air. However, sorbent regeneration is problematic for complex mixtures of odor chemicals and/or chemically active impregnates [28].

Carbonaceous adsorbents are very effective and one of the most commonly used adsorbents for hydrogen sulfide adsorption. One drawback of carbonaceous adsorbents is the lack of specificity they show when treating complex gas mixtures. This leads to rapid fouling. However, these sorbents can be processed via surface modification to more specifically target a plethora of different compounds. For the purpose of treating fecal pyrolysis exhaust, adsorption might work best as a polishing step to ensure that hydrogen sulfide is sufficiently low.

Many factors affect the adsorption capacity of carbon based adsorbents for hydrogen sulfide. These factors include the specific surface area, pore size distribution, pore volume, and surface chemistry. Higher surface area generally correlates with more space for both physical adsorption and catalysis. Concurrently, higher pore volume provides increased catalytic space for the oxidation of hydrogen sulfide. However, Bandosz [29] and Feng et al. [30] found that carbons with both micropores and mesopores are more effective for hydrogen sulfide oxidation than carbons with more micropores and higher surface area. It has been hypothesized that this is because mesopores allow for greater diffusion to active sites and prevent these active sites from getting blocked [31]. Surface chemistry affects adsorption due to how it interacts with the adsorbate. Heteroatoms such as oxygen, nitrogen, phosphorous, and hydrogen are commonly found on carbon surfaces and affect adsorption capacity through their influence on pH. For instance, a basic environment has been shown to enhance hydrogen sulfide adsorption because of the acidic nature of hydrogen sulfide [32]. Functional groups affect adsorption capacity through their interaction with the gas target. They can interact through both physical adsorption and chemisorption. In the case of hydrogen sulfide, humidity is another important factor. While adsorption capacity for most gas compounds is negatively impacted by high concentrations of water vapor, results consistently show that high relative humidity enhance the adsorption capacity of adsorbents for hydrogen sulfide. This is a result of the proposed reaction mechanism. **Table 3** summarizes the chemical and physical properties that impact hydrogen sulfide adsorption onto carbonaceous adsorbents.

Traditionally, activated carbon (AC) has been an effective adsorbent for low concentrations of hydrogen sulfide. It is inexpensive compared to other common adsorbents such as zeolite, alumina and silica. AC is biomass processed to have incredibly high surface area. The carbonization procedure eliminates any non-carbon species present in the biomass, producing

fixed carbon with a rudimentary pore structure. The activation process then enriches the pore volume by creating new porosity on the carbon surface. One gram of activated carbon has a surface area upwards of 500 m^2. Scientists speculate that the carbon pore surface, in conjunction with oxygen catalyzes the oxidation of hydrogen sulfide into elemental sulfur or other highly oxidized forms of sulfur. Hedden et al (1976) [34], proposed the following reaction mechanism. Water is

Table 3- Chemical and Physical characteristics impacting hydrogen sulfide adsorption onto carbonaceous adsorbents

Characteristic	Role
Pore size distribution [29]	A combination of micropores & mesopores allows for better pore access
Surface Area, Pore Volume	Space for physical adsorption & catalysis
pH	A basic pH encourages the formation of SH^- and catalytic oxidation to S
Surface chemistry	Interacts with the hydrogen sulfide through both physical & chemisorption
Humidity [33]	Humidity increases catalysis by providing a layer for hydrogen sulfide and oxygen dissociation
Gas Composition [32]	Oxygen increases catalysis through interactions with HS^-

adsorbed onto activated carbon. Hydrogen sulfide and oxygen dissolve into this water. The oxygen breaks down into radicals, which react with dissolved hydrosulfide ions, forming elemental sulfur and water.

While it is usually surface area that determines the effectiveness of AC during adsorption reactions, Ghosh et al. (2006) [35], found that high pore volumes, not high surface area achieved

higher reaction rates for AC with hydrogen sulfide. Because of the proposed mechanism, gas composition has a large effect on hydrogen sulfide adsorption. Both oxygen and humidity are crucial for the catalytic oxidation of hydrogen sulfide to elemental sulfur and sulfate. However studies have shown that during dry anoxic conditions, the hydrogen sulfide is oxidized by nitrogen and carbon dioxide, revealing the intrinsic capacity of carbon to oxidize sulfur compounds [33].

The local pH in the pore system has a substantial effect on the rate of hydrogen sulfide dissociation and its subsequent oxidation to various sulfur species. A moderately low pH in the pore system is projected to suppress the dissociation of H_2S and thus the creation of hydrogen sulfide ions. However, those ions that are formed are present at a lower concentration in small pores, leading to their oxidation to sulfur oxides and making the eventual formation of sulfate more favorable [36]. On the other hand, a more basic environment stimulates the dissociation of H_2S. This results in a high concentration of HS^- ions which favors their oxidation to chain or ring-like sulfur polymers. A pH value that is very low limits adsorbent/adsorbate interactions to physical adsorption [36].

Historically, activated carbon has been impregnated with caustic, such as NaOH, KOH, K_2CO_3 or KMnO4, enhancing the loading capacity and chemical adsorption. The result is the irreversible oxidation of hydrogen sulfide to elemental sulfur. NaOH impregnation has been shown to be one of the most effective alkaline activation options for optimal hydrogen sulfide removal [37]. Breakthrough capacity in general ranges from 120-220 mg H_2S/g Carbon. However, caustic impregnated carbons have many disadvantages, and researchers are looking to phase out their use. The concerns include: low ignition temperature; safety issues associated with handling caustic compounds; difficulty regenerating fouled carbons; and low physical adsorption capacity.

Researchers have been exploring the use of unimpregnated activated carbons for hydrogen sulfide adsorption. Unimpregnated activated carbon has proven very effective. Bandosz [32] found that the breakthrough capacity for the AC tested ranged from 5-295 mg H_2S/g carbon.

Biochar is another alternative to AC. Biochar and Activated Carbon differ in their preparation method, source material, and physiochemical properties. In contrast to AC, the use of biochar could be a cheaper remediation technology. The mechanism for biochar production requires far less energy than the production of AC. More importantly, the source material for biochar production can be extracted from waste streams and is essentially free.

A number of wood based biochars have been examined for their effectiveness in treating gas streams for hydrogen sulfide. Camphor derived biochar was shown to be an effective hydrogen sulfide adsorbent by Shang et al. [38]. The breakthrough capacity of the chars tested ranged from 35-383 mg H_2S/g char. Surface pH appeared to play a dominant role. In another study, it was found that Biochar was a cost effective replacement for unimpregnated AC, with biochar performance increasing in order as follows: unimpregnated activated carbon, camphor biochar, bamboo biochar, and rice hull biochar [39]. The proposed reaction mechanism for these biochars is shown below in **Equation 1**.

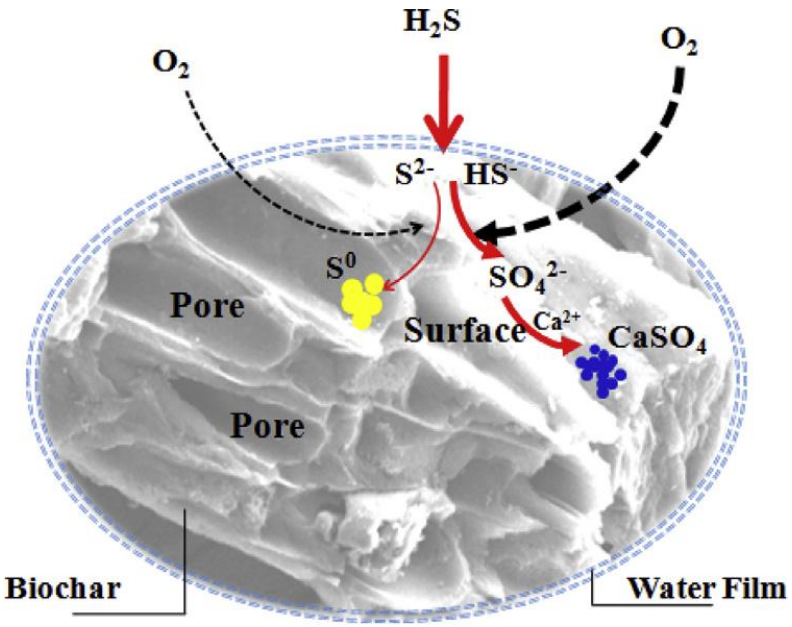
Equation 1 - Proposed reaction mechanism for the oxidation of hydrogen sulfide at the surface of biochar taken from Shang et al. [39]

$$H_2S_{gas} \overrightarrow{K_H} H_2S_{ads}$$
$$H_2S_{ads} \overrightarrow{K_s} H_2S_{ads-liq}$$
$$H_2S_{ads-liq} \overrightarrow{K_a} HS^-_{ads} + H^+$$
$$H^+_{ads} + O^*_{ads} \overrightarrow{K_{R1}} S_{ads} + OH^-$$
$$H^+_{ads} + 3O^*_{ads} \overrightarrow{K_{R2}} SO_{2ads} + OH^-$$
$$SO_{2ads} + O^*_{ads} + H_2O_{ads} \overrightarrow{K_{R3}} H_2SO_{4ads}$$
$$H^+ + OH^- \longrightarrow H_2O$$

In addition, many sewage sludge based chars have recently been characterized for their effectiveness at adsorbing hydrogen sulfide. Ros et al. [40], and Bandosz et al. [41] found that sludge with higher levels of iron, calcium and other alkali earth metals from the sludge treatment process had high capacities due to elevated pH. Pig manure derived biochar was found to perform even better than sewage sludge, and both promoted the complete oxidation of hydrogen sulfide to sulfate [42]. The range for these sewage sludge and pig manure derived chars was 47-66 mg H_2S/g char. The proposed mechanism for pig manure-derived biochar is illustrated in

Figure *3*. As of yet, raw human feces has not been explored for its utility as a hydrogen sulfide adsorbent. In the case of the Sol-Char toilet, the possibility of using feces-derived biochar for the management of fecal pyrolysis exhaust enhances the attractiveness of adsorption as a possible treatment technique.

Figure 3- Diagram of hydrogen sulfide adsorption and catalysis on pig manure-derived biochar taken from Xu et al. [42]



2.4.4. Biofiltration

Traditional technologies such as catalytic oxidation, chemical scrubbing and adsorption are effective for treatment of hydrogen sulfide, but have not proven as effective at dealing with odorous mixtures and in some instances serve only to concentrate instead of eliminate contaminants [43]. Biofiltration represents an alternative that eliminates rather than concentrates, uses low cost materials, has an extended lifetime, and is low maintenance. However, the effectiveness of bio-filtration relies on the biofilter design. Temperature, media consistency, media composition, moisture content, buffering capacity, nutrient content, bacterial community, and filter size are all important. Despite the delicate balance that must be maintained, it is possible to design a resilient system that sustains itself.

Biofilter Material

Common biofilter materials include soil, mixtures of compost material, and synthetic materials. Organic material such as wood chips and straw can function as well. Each media has advantages and disadvantages, but most variations work effectively to control odor from hydrogen sulfide as well as to break down organic contaminants. Microbes can function within a biofilm or distributed throughout a porous media such as soil [44]. Good support material generally have high void space, high surface area to volume ratio, low gas phase pressure drop, hydrophilic surfaces to maintain moisture content, low density, and low cost [45].

Soil and compost filters are classified as earth filters and offer many advantages over synthesized filter media. Gases (H_2S, SO_2, NH_3, NO_3, and many other contaminants) passing through these media are sorbed and oxidized to carbon dioxide water, sulfate and nitrogen. These filters are non-specific and typically adjust to available substrates [45]. Over the past 30 years soil bed filtration has been applied at full scale not only for odor abatement, but for the treatment of

exhaust gases and VOCs [44]. Acceptance of the system has followed an understanding of optimization of system parameters.

Synthetic media made with ceramics plastics or other material has become popular for higher concentrations of odor contaminants. These materials usually take the form of high surface area pellets and may be coated in activated carbon to enhance adsorption [46]. Because these media are synthesized, they must be supplied with buffers and nutrients to support microbial growth. For the purposes of a stand-alone toilet that must be low maintenance, these requirements seem unreasonable.

Soil and compost filters differ in many aspects. Soil filters have lower microbial population, require no additions to the filter material due to their natural buffering capacity and nutrient content, support plant growth, and are better suited to lower concentrations of pollutants [45]. Compost filters have to be replaced more frequently due to the normal decay process and mineralization, must be charged with a base or lime to deal with inorganic gases, have higher microbial populations, have higher air conductivity, are more susceptible to drying and require shallow beds to prevent compaction [45]. Due to the desire to create an odor control module that has little or no maintenance requirements, soil was chosen as the most promising filter media.

In terms of the supporting materials, soils were historically the first filter medium chosen for a biofilter. However, they were found to be prone to short-circuiting and clogging, which limited their historical use [47]. In addition, the lower microbial population relative to compost makes a larger footprint necessary for effective biofiltration [46]. However, over the last 30 years, recent studies and large scale trials have shown that soil biofilters can effectively control odor, even when odor is present at high intensities [48]. Earth filters made of either compost or soil provide structural support sorption surfaces, nutrients and water to maintain a healthy microbial

community. The natural nitrogen, phosphorous, and sulfur cycles help to maintain nutrient content in soils while compost media must be replaced regularly or supplemented with nutrients [45]. In addition, buffering capacity for variable and high concentrations of a contaminant has been enhanced in natural media by the use of activated carbon, which adsorbs contaminants when concentrations are too high to deal with biologically [46].

Based on the advantages of soil and compost filters, they were further researched. The key factors impacting the performance of soil and compost based biofilters are expanded upon below.

Sulfur Oxidizing Bacteria

While microorganisms may not be necessary for S transformations, they are responsible for the majority of oxidation and reduction reactions in soil and compost based biofilters [49]. While seeding has been discussed as an effective way to ensure media material has sufficient sulfur oxidizing bacteria, it is usually not necessary. Sulfur oxidizing microorganisms are ubiquitous in most soils, so their numbers rarely limit oxidation [50]. Instead, oxidation is limited by substrate availability. Heterotrophic oxidizers carry out the majority of S oxidation and require organic carbon to fulfill energy and carbon needs [50]. In the absence of sufficient organic carbon, autotrophic microbes, including those in the genus *Thiobacillu*s, play a larger role [51]. They obtain their energy from inorganic S and their C from carbon dioxide. The number of microbes responsible for oxidizing sulfur is tremendous, leading to variable biofilter populations based on variable substrates and designs.

The microorganisms responsible for sulfur oxidation are highly tolerant of soil acidity and low pH [51]. Inorganic gases such as hydrogen sulfide are oxidized to acids which subsequently need to react with alkaline substances. Biofilter media must have sufficient buffering capacity or

base content to support these reactions [45]. Soils have been shown to have an innate buffering capacity, though the buffering ability may not be capable of handling consistent high loads.

Moisture Content

Filter media moisture content is critical for effective odor reduction, with higher moisture levels being associated with higher removal efficiency [52]. Moisture is necessary for microbial activity as well as effective sorption [53], but the required moisture content depends heavily on the media consistency. Certain media choices retain moisture more effectively while other media are more prone to drying and thus failing. There is a balance, as too much moisture can also negatively impact filter effectiveness [54]. For compost filters a moisture content of 20-40% on a dry weight basis is recommended while for soil filters the number is estimated to be closer to 10-20% [53]. Humidified air can also enhance the efficiency of biofilters [48]. After their diffusion, pollutants enter the aqueous phase (absorption), making them bioavailable. Absorption represents an important mechanism for pollutant removal in biofilters when pollutants are soluble [48].

Temperature

In the case of earth filters, gas temperature and microbial metabolism ensure filter function even at low ambient temperatures [45]. However, the temperature fluctuations associated with the gas stream and ambient conditions does influence removal efficiency. At temperatures of 35°C removal was 10% higher than at 29°C [53].

Design Parameters

Contact time and air flow, two of the most important design parameters, are a result of how biofilters are sized. Contact time is important to ensure sufficient removal of hydrogen sulfide and will also vary based on the porosity of the media [55]. The reaction rate is dependent on both diffusion and degradation, which are in turn dependent on the solubility and concentration of the

contaminant [44]. Another consideration is how to ensure that contaminants are evenly distributed through filter media. Once that is achieved optimal removal will depend on the contaminant load per unit time and the degradation capacity of the microbial community in pollutant load per unit media volume per unit time [44].

Pressure drops associated with flow rates are a common issue associated with biofiltration. A pressure drop is noteworthy when is exceeds 22-30 cm of water per meter of bed depth [48]. Soil filters, which are more compact, require lower air flow rates to avoid meeting this limit than compost filters, which are more porous [48]. Step-fed biofilters, in which air is fed in at multiple heights in the biofilter, decrease pressure drop buildups, increasing the packing material's lifetime [56].

2.4.5. Biofiltration Combined with Adsorption

Both adsorption and biofiltration have been effectively used to eliminate odor for years. Newer research has looked at the effectiveness of combining the two. There are multiple examples of using activated carbon in conjunction with biofilters to enhance odor control. The advantage of systems combining both seems to be low moisture demand, low pressure drop, and high biofilm stability [57]. GAC is an effective packing material because it allows for rapid pollutant adsorption followed by release for biodegradation. A dynamic equilibrium can be reached between adsorption and biodegradation, leading to steady state efficiency [57]. Taken all together, the literature indicates that a biochar enhanced soil filter may serve as a resilient, sustainable solution to high concentrations of hydrogen sulfide and intermittent fecal odor.

Most biochar trials have been done on acidic soils, where biochars with pH between 6 and 10 were used. Many studies have compared the effect of adding biochar to acidic and alkaline soil and all found greater benefits on crop growth in the acidic soil [58-60]. Thus, the addition of

biochar may be a way to counteract the acidification of soil due to oxidation of hydrogen sulfide to sulfate via microbial metabolism.

3. Odor & Hydrogen Sulfide Quantification during Fecal Pyrolysis

3.1. Methods

In order to create an odor treatment module for the management of fecal pyrolysis exhaust, the expected odor and hydrogen sulfide concentrations had to be characterized. This chapter of the thesis summarizes the experiments used to characterize both as well as the results of these experiments.

3.1.1. Sample Collection

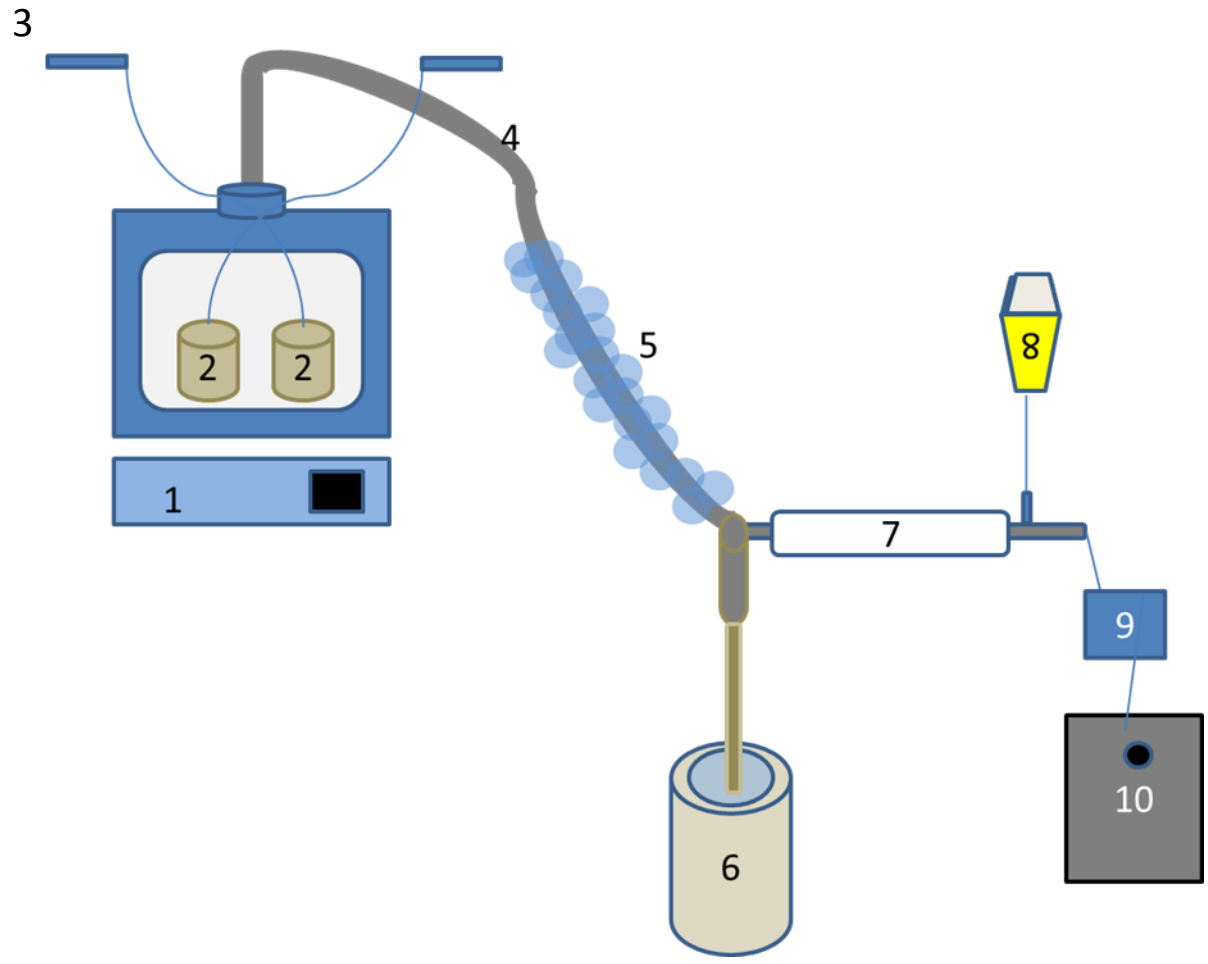
Char samples used to conduct this research were derived from wood biochar and real human feces. The researchers involved in the Reinvent the Toilet Challenge project obtained permission to collect and process real human waste for this study. Most of the human waste used for these experiments was collected from the CU student population on a voluntary basis and stored frozen until needed. The samples were stored in either stainless steel or ceramic containers. These containers were then sealed in plastic buckets to provide a second barrier to the environment. The amount of sample collected ranged from 40 -250 grams per stool.

3.1.2. Experimental Setup

Fecal char was created using a Thermolene Scientific Type F600 muffle furnace. Fecal samples were placed in lidded ceramic containers in order to ensure a low oxygen pyrolysis environment and were pyrolyzed two at a time. Type K thermocouples were used to monitor both samples as well as the oven temperature and data was logged using EasyLog USB data loggers. To quantify the release of odor and hydrogen sulfide it was necessary to divert and scrub the fecal exhaust gas. Stainless steel flanges and pipes were used to direct the exhaust stream out of the oven. The humidity of the gas stream was monitored using an Omega RH-USB probe before being piped through aluminum tubing that was cooled using ice and water. The liquids were condensed in this way in order to prevent humidity and tars from interfering with the performance of the

chemical sensors. Condensed liquids were allowed to flow into a water trap. The gas was then passed through a fourteen inch glass column filled with cotton in order to filter out any particulate matter or residual tar. The exhaust was finally split into two streams so that both odor samples and real time hydrogen sulfide measurements could be taken at the same time. A schematic of the experimental setup is shown in **Figure 4**.

Figure 4- Setup for the quantification of hydrogen sulfide and odor during fecal pyrolysis. *1) Muffle Furnace 2) Ceramic containers with fecal samples 3) Thermocouples 4) Stainless steel pipes 5) Aluminum tubing with cooling apparatus 6) Liquids trap7) Cotton filter 8) Hydrogen sulfide monitor 9) Air pump 10) Grab bag*



3.1.3. Quantification Equipment & Data Collection

Odor samples were collected using an SKC 1 L/min grab air sampling pump, 10 L Standard FlexFoil bags, and PTFE tubing. The sample bags were chosen because they effectively retain hydrogen sulfide for up to 48 hours, provide good light and moisture barriers, and also retain carbon monoxide, carbon dioxide, methane, hydrogen, carbonyl sulfide, methyl and ethyl mercaptan, and sulfur hexafluoride. Odor samples were taken when hydrogen sulfide levels were peaking. Due to the strong odor associated with the exhaust, grab samples were pre-diluted 1:30,000 using the Scentroid SM100 dynamic olfactometer.

A Scentroid SM100 dynamic olfactometer and a panel of 6 human test subjects were then used to quantify the odor units of the fecal pyrolysis exhaust samples. The olfactometer draws in air from sample bags using a vacuum pump and then dilutes the sample using compressed air. The ratio of sample to compressed air is controlled by an adjustable sliding valve with the position of the valve correlating to a specific odor unit in OU/m^3.

Hydrogen sulfide was detected using a Honeywell GasAlertMicro5 IR chemical sensor with a sensitivity of 1 ppm and a range of 0-500 ppm. The effects of varying temperature and ramp rate on hydrogen sulfide release were monitored.

After each experiment, pyrolyzed char was ground down using standard Tyler sieves. The char was ground down to 0.3-0.4mm. Literature indicates that this is the best biochar size to use for hydrogen sulfide adsorption by biochar in gas streams [38].

3.2. Results & Discussion

3.2.1. Odor Quantification

The odor detection threshold was calculated using an odor panel of individuals. The odor threshold is defined as the point at which half of an odor panel are able to perceive a change in odor. In the case of fecal pyrolysis exhaust, half of the panelists detected an odor by valve position

8. The valve position when odor was detected for each panelist is listed in **Table 4**. Position 8 correlates to 17 OU/m^3.

Table 4- Fecal Pyrolysis Exhaust Odor Threshold

Panelist	Valve Position at Detection	Corresponding Odor Units (OU/m^3)	Odor Units Without Dilution (OU/m^3)
Observer 1	8	17	510,000
Observer 2	10	9	270,000
Observer 3	10	9	270,000
Observer 4	*DNS	*DNS	*DNS
Observer 5	5	28	840,000
Observer 6	7	19	570,000

*DNS- Did Not Smell

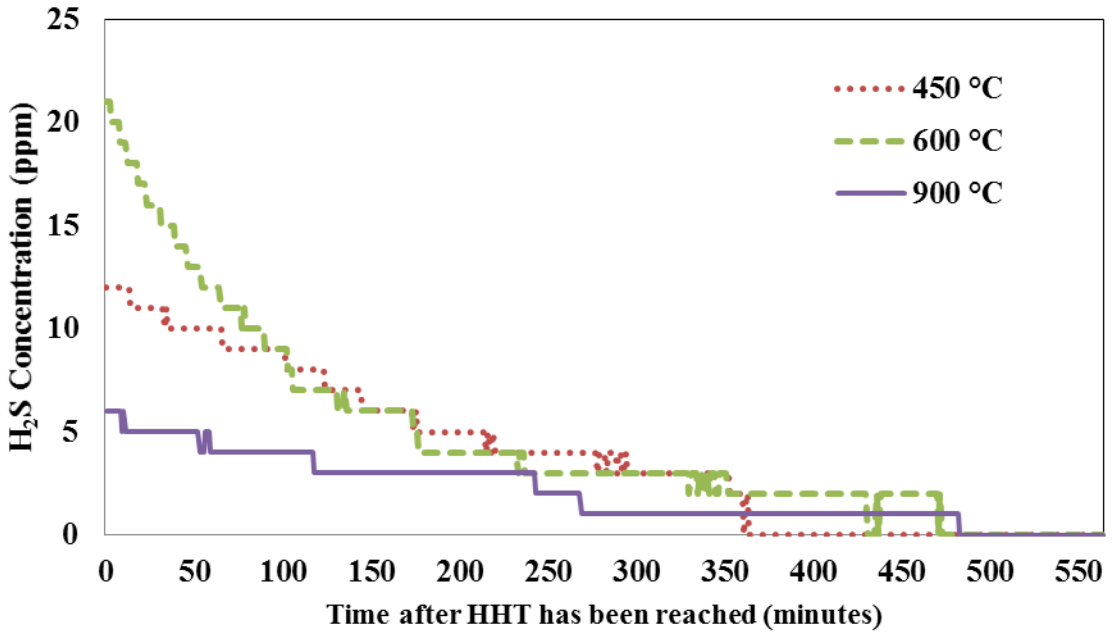
An odor detection threshold of 510,000 odor units per m^3 was determined using the perceived odor threshold as well as the pre-dilution ratio of 1:30000. Odor index data from St. Croix Sensory, a sensory testing and training company, correlates rendering plant uncontrolled exhaust with 1,000,000 OU/m^3 and venting anaerobic digester gases with 100,000 OU/m^3 [61]. This establishes 510,000 OU/m^3 as a very reasonable detection threshold level for fecal pyrolysis exhaust. The above test was conducted using an exhaust sample with a measured hydrogen sulfide concentration of 32 ppm. At the odor threshold the hydrogen sulfide concentration has been diluted to .0627 ppb. The detection threshold for hydrogen sulfide gas has been placed at approximately .00047 ppb. This indicates that hydrogen sulfide is not the lowest detection threshold compound or that there may be a synergistic effect between compounds in the exhaust, making it overall more odorous than the lowest detection threshold compound on its own.

3.2.2. H_2S Quantification

Based on the variation in ramp rate and highest heating temperature, many observations regarding hydrogen sulfide release could be made.

Figure 5 below shows the hydrogen sulfide concentration following the char reaching its highest heating temperature (HHT).

Figure 5- Quantification of hydrogen sulfide after different highest heating temperatures have been reached.



For this figure, the ramp rate was an increase in temperature of 5 ºC per minute. The x-axis shows the number of minutes after the internal char sample has reached the highest heating rate. There is a delay between when the oven reached this temperature and when the char reached this temperature. Because three different temperatures are examined in this graph, it is important to note that the number of minutes prior to each char reaching its peak pyrolysis temperature varied, with the amount of time required increasing with increasing temperature. The y-axis shows the concentration of hydrogen sulfide. The graph shows that the peak release of hydrogen sulfide occurs at or prior to the HHT being reached. For all three HHTs, the concentration of hydrogen sulfide is declining when the temperature stabilizes. Intuitively, the lower the HHT, the higher the

expected concentration of hydrogen sulfide when the HHT is reached. This is because at higher heating temperatures, the fecal samples have been at high heat for a much longer period of time before reaching the HHT. This means that the hydrogen sulfide has had much longer to be released as part of the pyrolysis exhaust. However, the concentration of hydrogen sulfide after HHT is reached is higher for the 600 °C run than for 450 ºC run. This may be the result of the low mass associated with the stool sample used for the 450 °C run. However, the mass of the stool sample used for the 600 ºC run is unknown, and further research needs to be conducted before any conclusions can be drawn. In addition, there is a natural variation in hydrogen sulfide concentration associated with stool samples.

Another obesrvation based on the charring experiments is how ramp rate affects the temperature at which peak hydrogen sulfide release occurs. **Figure 6** shows hydrogen sulfide peaks for different ramp rates of 1 °C, 3 °C, and 5 °C.

For these observations, the experiments with 1 °C and 3 °C ramp rates were run with a highest heating temperature of 300 °C, while the 5 °C ramp rate experiment was run with a highest heating temperature of 600 °C. The disparity in the temperatures where the ramp rates end is based on the need to go beyond the temperature of 300 °C in the case of the 5 °C ramp to achieve the peak hydrogen sulfide for the experiment. For **Figure 6,** the x-axis shows the internal char temperature. Looking at the graph, it is evident that as ramp rate increases, the peak hydrogen sulfide level occurs at a higher temperature. However, it is important to note that these temperatures do not correlate with time and higher temperatures are reached more quickly when a higher ramp rate is used. For the 1 °C ramp rate the peak was reached at 117 minutes. The maximum hydrogen sulfide concetration for the experiment with a 3 °C ramp rate was reached at 99 minutes. Finally, for the 5 °C ramp rate, the maximun hyrogen sulfide concentration was

reached at 82 minutes. This shows that a higher ramp rate, which leads to higher temperatures being achieved more quickly. leads to the faster release of hydrogen sulfide, and thus the H_2S peak occurs at a higher temperature.

Figure 6-The effect of varying ramp rate on hydrogen sulfide release

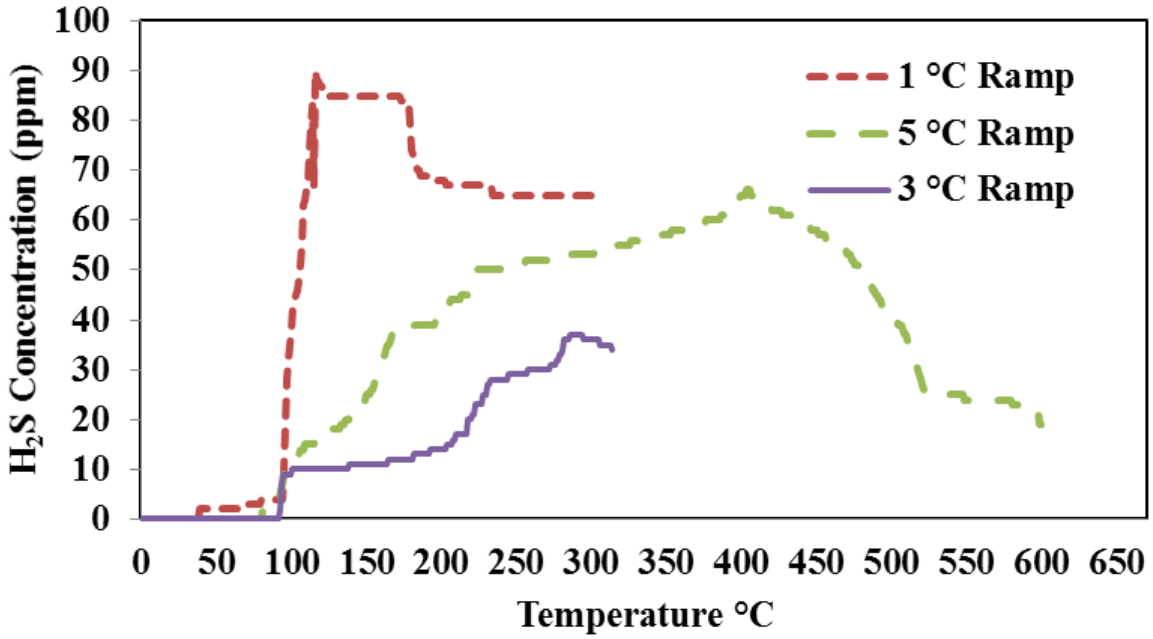
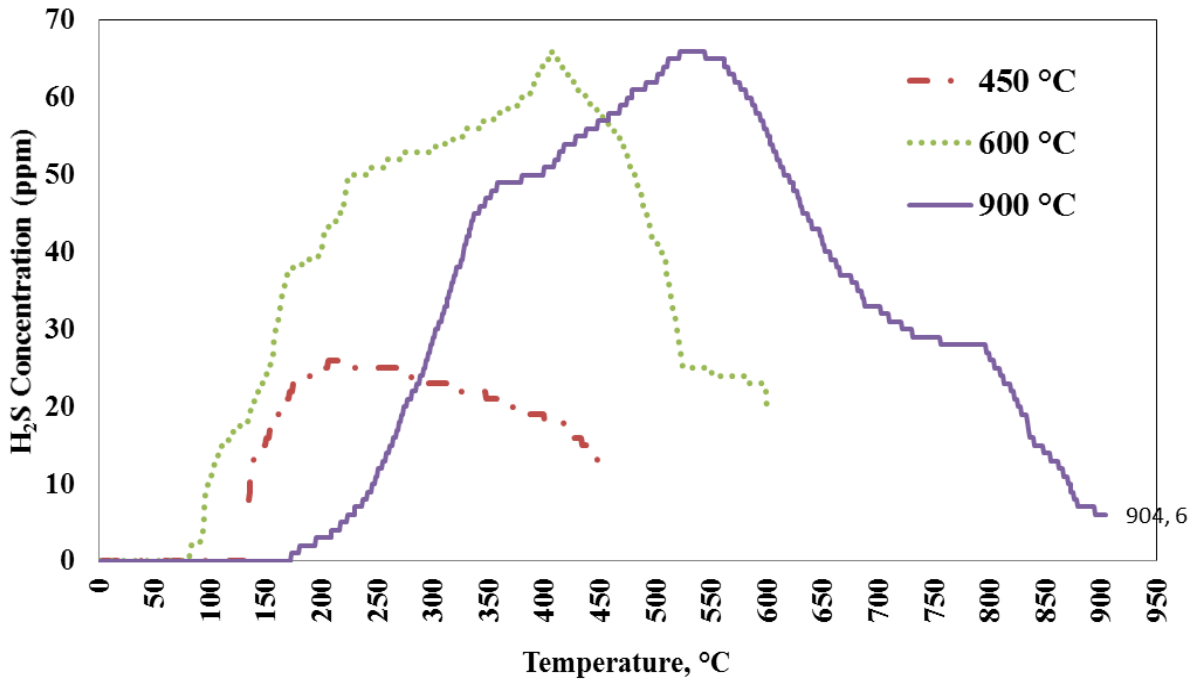


Figure 7 below shows how increasing the highest heating temperature affects hydrogen sulfide release. Ramp rate was held at 5K for each of the runs shown. The x-axis shows the internal temperature of the char, while the y-axis shows the hydrogen sulfide concentration at that temperature.

Because the ramp rates are the same, you would expect the three different runs to mirror eachother. However, the peak hydrogen sulfide release occurs at higher temperatures as you increase the highest heating temperature. To interpret what this indicates it is important to remember that the there is a lag between the oven temperature and the internal char temperature. Ths means that the

point at which the hydrogen sulfide peaks are occuring is close to the point where the temperature stabalizes at the highest heating temperature. The movement of the peaks to the right as the HHT increaeses indicates that the increase in temperature is causing the release of hydrogen sulfide that would not have been release at lower HHTs. This is not unexpected, as the peak temperature and ramp rate impact the yield of syngas, as well as the qualities of char produced. Pyrolysis at moderate temperatures of 400 – 600 °C is called fast pyrolysis and it produces 50-70% bio-oil, 10-30% biochar, and 15-20% syngas. Syngas production is optimized through fast pyrolysis gasification, which operate at temperatures between 800 and 1200°C and produces very little biochar or bio-oil [11].

Figure 7- The relationship between increasing peak pyrolysis temperature and the release of hydrogen sulfide



Fecal sulfide concentrations range from 0.17–3.38 mmol/kg [62]. Diet, among other factors, influences the amount of hydrogen sulfide in human feces [63]. Based on the range

described above, the expected concentration range of H_2S in feces is 0.58-115.26 µg H_2S/g feces. Based on the range in the amount of stool used for each quantification experiment, the expected total H_2S release varies between 0.464-57.6 milligrams. To compare the amount of H_2S in feces to the amount of H_2S released during fecal pyrolysis, a rough calculation of the amount of hydrogen sulfide released for pyrolysis runs made at four different temperatures and at two different ramp rates were made. The flow rate of the exhaust was estimated based on a few measurements with a low accuracy anemometer and the pipe diameter size. Flow rate was expected to vary at different temperatures because of the increase in syngas production at higher temperatures and that is reflected in the estimated flow rates. For simplicity, an average flow rates was used for calculations, but in reality, the flow would vary throughout the pyrolysis process.

Looking at **Table 5**, it appears there is a trend towards increasing hydrogen sulfide release with increasing temperature. This aligns with the above hypothesis that increasing the temperature of pyrolysis leads to the release of more hydrogen sulfide than would have been released at lower

Table 5 - The total release of Hydrogen sulfide during select charring experiments; the total release of hydrogen sulfide normalized by stool mass for select charring experiments

	300 °C, 1 K	**450 °C, 5 K**	**600 °C, 5 K**	**900 °C, 5 K**
Theoretical Gas Flow (L/min)	1	1.73	2	4
Calculated Total H_2S (g)	.0366	.0119	.0229	.0521
Volume normalized by Stool Mass (g/g)	.0000799	.0000882	*DNR	*DNR

*DNR-Did not record

temperatures. The exception to this trend is the 300 °C experiment. A much larger amount of hydrogen sulfide was released during this experiment. This may be explained by either the lower ramp rate, or the higher mass associated with these stool samples. For the 300 °C and 450 °C

samples normalizing the samples by the mass of the samples causes these different temperatures to align more specifically with the other samples. However, because there is limited data on how hydrogen sulfide release correlates with the mass of the samples pyrolyzed, it is difficult to draw conclusions. In addition, data on the mass of the pyrolyzed stool was not consistently collected. Understanding these trends is compounded by the natural variation in concentration from stool sample to stool sample. That said, the numbers above are within the range mentioned previously for the concentration of hydrogen sulfide in feces, and they tend to reach the upper limit of that range as temperature increases. The results seem intuitively to make sense, as more of the biomass is converted to syngas over biochar or bio-oil at higher pyrolysis temperatures.

4. Odor and Hydrogen Sulfide Treatment: Adsorption

This chapter details the results from experiments used to characterize the effectiveness of different biochars as adsorbents for the treatment of the sol-char fecal pyrolysis exhaust stream as well as other industrial gas streams that require treatment for hydrogen sulfide. Biochars derived from human feces were examined for their ability to remove hydrogen sulfide from gas streams. Feces-based adsorbents were pyrolyzed at temperatures of 300 °C, 450 °C, and 900 °C in a low oxygen environment. These adsorbents were characterized before and after static breakthrough tests using nitrogen sorption tests, surface pH tests, elemental analysis, SEM-EDS, FTIR, and IC. It was found that feces-derived biochar has potential as a hydrogen sulfide adsorbent and that high temperature feces- derived biochars outperform low temperature biochars. Surface data indicate that the enhanced fraction of alkali metals leading to higher surface pH, a higher surface area, and the presence of micropores are likely to contribute to the increased capacity of high temperature fecal chars.

Wood and bamboo based chars were examined under the same empirical conditions using the same analytical tools and compared to feces-based chars for their effectiveness as hydrogen sulfide adsorbents. Results indicate that at these conditions, feces-derived biochars are superior to wood or bamboo based chars for this purpose.

4.1. Introduction

Hydrogen sulfide is a nuisance gas produced as a result of both natural and anthropogenic processes. Due to its negative health and environmental impacts and characteristic rotten egg odor, it’s a common target for removal in industries such as wastewater treatment and petrochemical processing [64]. Chemisorption onto caustic impregnated activated carbon (AC) is a frequently used pollution control mechanism for its removal at low concentrations [65]. However, a low

temperature of ignition, the irreversible nature of chemisorption, and the dangers associated with handling caustic solutions have compelled a search for alternative adsorbents. Unimpregnated activated carbon and a variety of biomass based biochars have been examined and found to be feasible substitutions [33, 39-42, 66-76]. AC and biochars diverge in their manner of preparation, their feedstock source, and their physiochemical characteristics. Biochar is less energy and cost intensive to prepare and consequently has been receiving a lot of attention as a cheap, sustainable AC alternative. Evidence suggests that the effectiveness of any of these carbonaceous sorbents for H_2S is due to an intrinsic ability to catalyze oxidation as well as its physical and chemical sorption capabilities [75]. Surface chemistry [32, 68], surface area, pore size distribution [30, 77, 78], and gas composition [33, 66, 69] combine to determine the efficiency of these adsorbents for hydrogen sulfide removal. While sewage sludge-derived char has been shown to be an effective H_2S adsorbent [40-42, 70, 79, 80], raw fecal sludge based biochar has never been assessed for this purpose. Alternative waste treatment options, including fecal pyrolysis, are currently being investigated for use in underdeveloped regions where the necessary infrastructure for traditional sewage sludge-based treatment technologies is not financially or geographically feasible [81]. The creation and use of fecal biochar as a hydrogen sulfide adsorbent is a potential way to both render human waste safe, which is essential for human health and safety, and also to transform it into a useful byproduct. This study aims to evaluate the potential of human feces-derived biochar for the adsorption of hydrogen sulfide. The heterogeneous nature of fecal sludge makes drawing specific conclusions about the nature of fecal char a challenge. However, understanding how pyrolysis temperature impacts the surface characteristics and relative adsorption capacities of chars can provide a baseline for understanding optimal fecal char properties for hydrogen sulfide adsorption.

4.2. Methods: Feces-Derived Chars

Fecal chars at pyrolysis temperatures of 300 °C, 450 °C, and 900 °C were created using a Thermolene Scientific Type F6000 muffle furnace. Samples were placed in lidded ceramic containers to ensure a low oxygen pyrolysis environment and were pyrolyzed at the highest heating temperature for 2 hours. Type K thermocouples were used to monitor both samples as well as the oven temperature. Each char was then ground down using a mortar and pestle and screened to particle sizes between 0.297-0.420 mm. Literature indicates that 0.3-0.4 mm is the optimal biochar particle size for hydrogen sulfide adsorption in gas streams [38].

4.2.1. Char Characterization

pH

The average pH of each biochar was measured to get information on the acidity and basicity of each sorbent. To do this, approximately 0.75 g of each sample was added to 15 mL of deionized water. The solution was then placed on a shaker at 200 rpm for twenty-four hours before being filtered using a syringe and 2 micron filter. The pH of the filtrate was then measured using a pH probe.

Sorption of Nitrogen

Brunauer–Emmett–Teller (BET) analysis was performed (USGS, Denver, Colorado) and the nitrogen isotherms were used to determine surface area, pore volume, and pore size distribution. The method uses a five-point N_2 gas adsorption technique (ASAP 2020, Micrometrics) and the relative pressure was run up to 0.98 ATM. Analysis was performed by Dave Rutherford at the Unites States Geological Survey Laboratory in Denver, Colorado. This analysis was useful because both surface area and pore volume correlate with the adsorption capacity of adsorbents. For analysis, 1 g samples were sent to the USGS.

Elemental Analysis

Wet digestion was performed by the North Carolina State University Department of Soil Science. Samples were diluted as needed and analyzed on a Perkin Elmer ICP-optical emission spectrometer 8000.The relative percentage of C, H, N as well as the concentration of S, Ca, Mg, Al, Mn, Cu, Zn, Fe, and K in each biochar were obtained.

SEM-EDS

SEM- EDS, or Scanning Electron Microscopy-Energy Dispersive Spectroscopy, was performed using an SEM JEOL JSM 6480LV machine with attached EDS. The interaction between electrons from the SEM and the atoms samples interact to produce various signals which can be used to create a topographic map. The EDS allows for the identification of particular surface elements using backscattered electron images that display differently for different atomic elements. The technology allowed for the identification of surface elements and provided a general idea of their relative proportions at the char surface.

PH

The pH of each biochar in solution was measured to get information on the acidity/basicity of each sorbent. Approximately 0.75 g of each char sample was added to 15 mL of deionized water. The solution was then placed on a shaker at 200 rpm for twenty-four hours before being filtered using a syringe and 2 micron filter. The pH of the filtrate was measured using a pH probe.

FTIR

Fourier-Transform Infrared (FTIR) spectroscopy was performed using a ThermoScientific Nicolet 3700 FTIR machine with an ATR attach and germanium crystal. The analysis provided information regarding how each biochar absorbs light, and was used to detect char surface functional groups. Spectra were obtained over 16 scans set at a resolution of 2 cm^{-1}, covering the

range of 4500–499 cm^{-1} and with an aperture size of 30 cm. The reflectance was measured and analyzed using OMNIC v7.1.

Soluble Sulfate Content

The amount of sulfate relative to the amount of H_2S passed through each char column was used to elucidate the oxidation pathway. Approximately 0.75 g of each sample was added to 15 mL of deionized water. The solution was then placed on a shaker at 200 rpm for twenty-four hours before being filtered using a syringe and 2 micron filter. Soluble anions in the filtrate, including sulfate, were then measured using a Dionex Ion Chromatography (IC) system operated with a sodium carbonate and sodium bicarbonate mix eluent (LEGS Laboratory, Department of Geological Sciences, and University of Colorado-Boulder).

4.2.2. Hydrogen Sulfide Breakthrough

Static Hydrogen Sulfide Breakthrough Experiments

Static breakthrough capacity tests were conducted at a flow rate of 200 standard cubic centimeters per minute, a hydrogen sulfide concentration of 90 ppm, and an oxygen level of 10.5 percent. Compressed air and compressed nitrogen with a hydrogen sulfide concentration of 180 ppm were mixed at a 1:1 ratio using an 1179A MKS Mass-Flo Controller and a GM50A MKS Mass-Flo Controller. Prior to testing, chars were wetted with 5 mL of water to ensure the presence of a water film [33, 66]. Hedden et al. [34] proposed that the mechanism for catalytic oxidation of hydrogen sulfide on carbon involves the dissociation into adsorbed water of HS^- and H^+ followed by oxidation via O_2^* or O_2. Thus a water film on chars is assumed to be important as a site for dissolved HS^- to react with chemisorbed O_2, and oxygen is assumed to be essential for catalytic oxidation. The low concentration of oxygen for this setup represents the concentration deemed sufficient for catalytic oxidation to occur. For each test, a volume of 12.4 mL of char was packed inside of an ace glass column using BIOTEC glass beads. Due to differences in bulk density, the

mass of the various chars used for each breakthrough experiment varied widely. Each biochar column had a height of 130 mm and a diameter of 11 mm. Hydrogen sulfide breakthrough concentrations were monitored using a GasAlertMicro5 IR chemical sensor and experiments were run at ambient room temperature. A schematic of the experimental setup is shown in **Figure 8**. Experiments were run until hydrogen sulfide concentrations stabilized. Breakthrough capacity was calculated using **Equation 2**.

Equation 2- Breakthrough Capacity

$$Breakthrough\ capacity = (H_2S) * F * \frac{T_{BT}}{V_C}$$

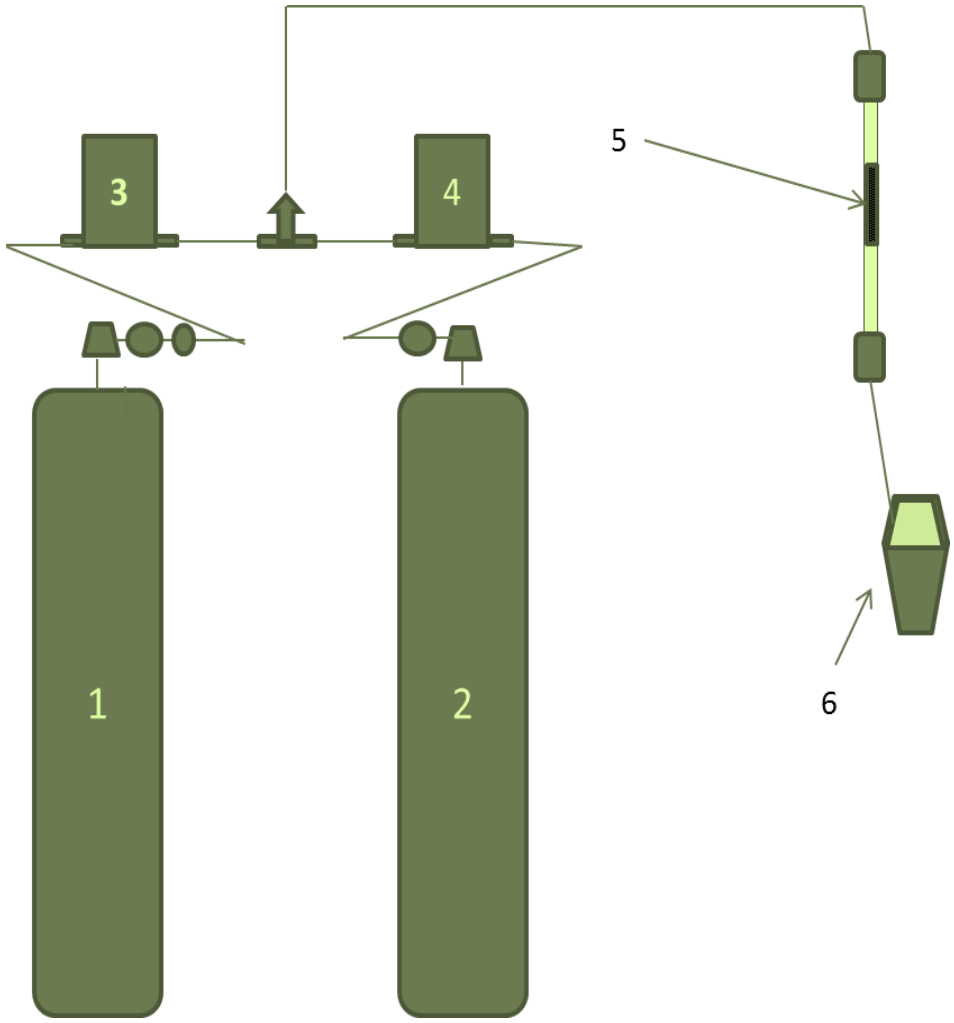
$$Where\ (H_2S) = Concentration\ in \frac{g}{ml}$$

$$F = Flow, in\ ml/min$$

$$T_{BT} = Break\ through\ time, in\ minutes$$

$$V_c = Volume\ of\ carbon, in\ ml$$

Figure 8-Experimental setup for hydrogen sulfide adsorption tests: 1) 180 ppm H_2S, balance N_2 2) Compressed Air 3) Mass-Flo Controller 4) Mass-Flo Controller 5) Adsorption column 6) Chemical hydrogen sulfide sensor



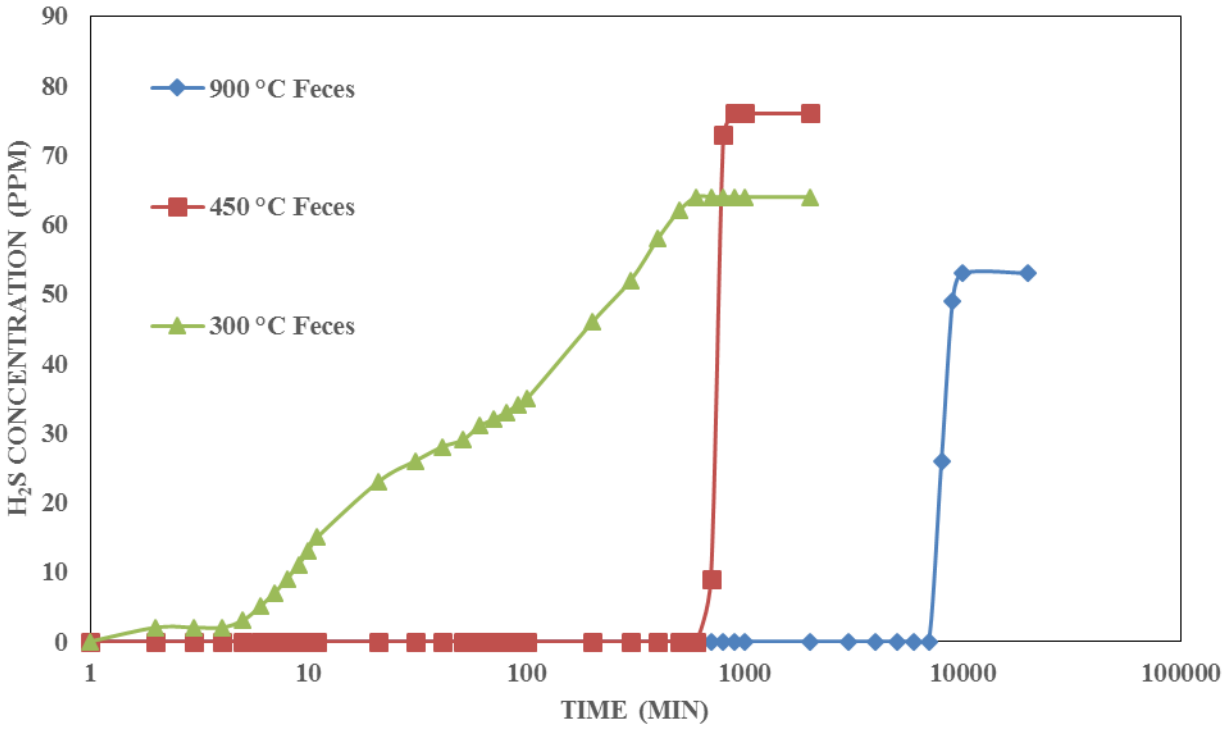
4.3. Results & Discussion- Feces-Derived Char

4.3.1. Hydrogen Sulfide Breakthrough

Breakthrough curves serve to validate the effectiveness of each adsorbent for hydrogen sulfide adsorption and to establish a breakthrough time during specific empirical conditions. The breakthrough curves for each char are shown in **Figure 9**. They are consistent with what would be

expected from carbonaceous adsorbents as a combination of adsorption and catalysis is responsible for steady state breakthrough at some fraction of the inlet concentration. [82] .

Figure 9-Hydrogen sulfide breakthrough curves for static breakthrough tests of feces-derived biochar created at different temperatures



For these experiments breakthrough was calculated as the time at which hydrogen sulfide was first detected. The calculated breakthrough capacities normalized by volume, mass, surface area, and pore volume are shown in **Table 6**. The hydrogen sulfide breakthrough capacity of fecal chars seems to increase with increasing temperature. Overall, the 900° C Fecal char

Table 6-- Calculated breakthrough capacities based on static breakthrough experiments and normalized by BET data

	Char (g)	Water (g)	Bulk Density (g/cm^3)	BT Mass (mg/g)	BT Volume (mg/cm3)	BT SA (mg/cm3)	BT PV (mg/cm3)	BT µPV (mg/cm3)
300 ° C Feces	5.92	5	.48	.007	.002	.009	1.488	2.231
450 ° C Feces	5.25	5	.42	3.493	1.485	.225	120.463	139.737
900 ° C Feces	6.11	5	.50	37.557	15.968	.359	398.403	586.739

*BT- breakthrough, SA- surface area, PV- pore volume, µ- micro

performed better than the lower temperature char and had a breakthrough capacity that outperformed the 450° C char by a factor or ten. The feces-based 300°C chars broke through within 5 minutes and had the lowest adsorption capacity. Interestingly, the high temperature chars outperformed the low temperature char despite the declines in basic functional groups associated with increasing pyrolysis temperature, most likely due to increased surface area and an increase in the fraction of inorganic minerals. Various factors such as the nature of the adsorbent, column geometry, gas flow rate, and gas composition affect the nature of breakthrough curves for hydrogen sulfide. It is possible that the low relative humidity and oxygen levels impacted the catalytic abilities of the chars differently.

4.3.2. Char Characterization

BET

With the exception of the 900 °C fecal char, the surface areas of these fecal biochar are low on the spectrum relative to other biomass-based biochars. Ultimately, breakthrough capacity relies on available pore space for catalysis to occur, and the 300°C fecal char did not have a sufficient amount. As expected, higher pyrolysis temperatures resulted in higher surface areas, higher pore volumes, and a better pore volume distribution. In the case of hydrogen sulfide adsorption, pore

size distribution is thought to play an important role [30, 77]. A combination of mesopores and micropores is desirable to ensure sufficient pore access. Micropores serve as low oxygen environment for the formation of elemental sulfur. In general, the breakthrough capacities of the chars increased with increasing surface area and pore volume. The 900 °C fecal char was the only char with a significant fraction of micropores and mesopores dominated for all chars. However, when breakthrough results were normalized by surface area and pore volume (**Error! Reference source not found.**), the trend of higher pyrolysis temperature leading to higher breakthrough capacity stands. This indicates that surface chemistry plays a crucial role, as none of the BET results fully explain the breakthrough trends. The data on breakthrough capacity is compile in **Table 7**.

Table 7- BET analysis of feces-derived chars

	Surface Area (m^2/g)	Pore Volume (cc/g)	Micropore Volume Fraction	Mesopore Volume Fraction	Macropore Volume Fraction
300 °C Feces	**0.5**	**0.003**	**0.01**	**0.57**	**0.42**
450°C Feces	**15.5**	**0.029**	**0**	**0.86**	**0.14**
900°C Feces	**89.9**	**0.081**	**0.26**	**0.68**	**0.06**

Elemental Analysis

Ash content is expected to be high for feces-derived chars. The is because the high inorganic matter present in fecal sludge catalyzes the volatilization of organics, leading to lower C, N, and H yields than would be obtained for chars with low inorganic content [83]. In human biomass based chars this results in a decrease in carbon content based on weight percentage and an increase in the percentage of various mineral elements. Previous studies using sewage sludge based adsorbents have shown that these may manifest as metal oxides, which can serve as active

elements for the catalysis of the oxidation of hydrogen sulfide [69, 84]. Overall, the alkali earth metal content increases and the C, N, and H yields decrease as pyrolysis temperature increases. This is due to the increased volitization of the organic fraction at higher temperatures. The inorganic alkali earth metals such as Ca and Mg have been shown to increase adsorption/oxidation of hydrogen sulfide through their effects on pH [85, 86]. Accordingly, the increase in breakthrough capacity as temperature increases can be tied to the increase in the inorganic fraction of these particular metals. The effects of feces peak pyrolysis temperature on elemental composition are shown in **Table 8**.

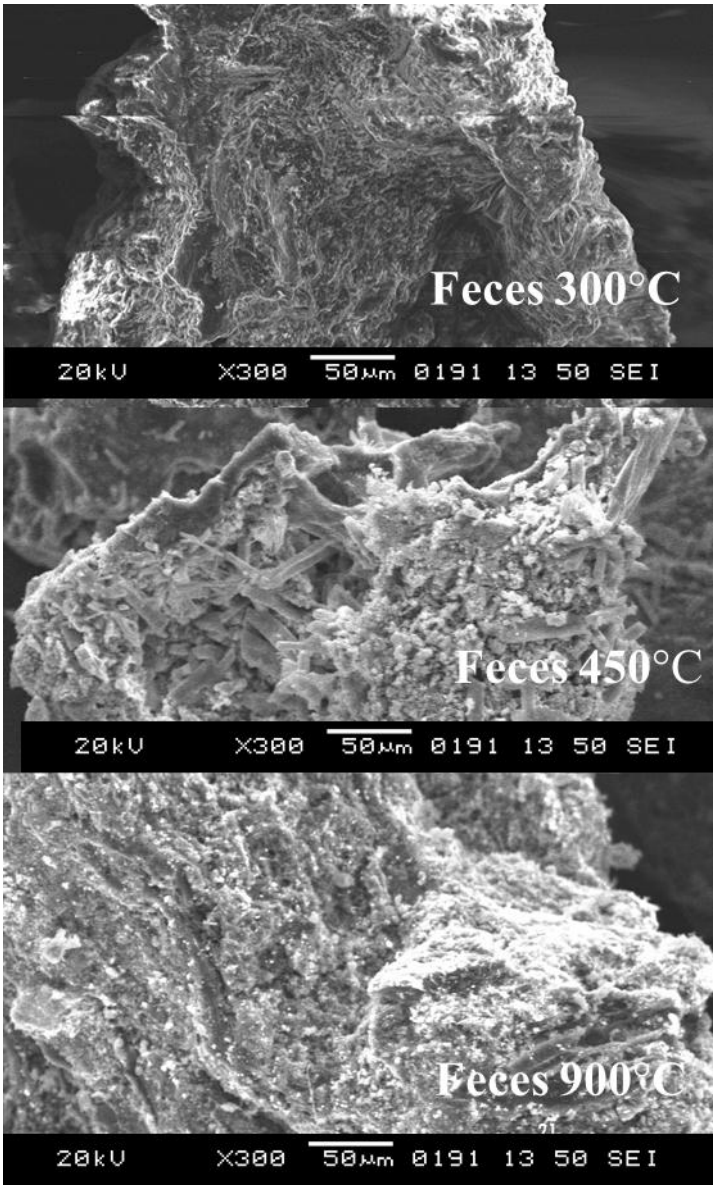
Table 8- Elemental analysis of feces-derived chars at various temperatures

	Ca	**K**	**Mg**	**S**	**Al**	**Cu**	**Fe**	**Mn**	**Zn**	C	**H**	**N**
	wt%	wt%	wt%	wt%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	% C	%H	% N
300	4.4	2.5	1.1	0.3	2358	70.2	810	250.9	365.4	49.7	4.6	5.1
450	6.4	5.3	1.8	0.2	1286	67.4	8217	350.4	696.3	39.2	1.7	4.1
900	10	6.2	2.8	0.1	751	63.9	2278	411.6	317.4	34.3	0.4	2.1

SEM-EDS

Scanning Electron Microscopy micrographs are shown in **Figure 10** Energy Dispersive Spectroscopy was used to identify particular surface elements and provide a general idea of

Figure 10- Scanning electron photographs of feces-derived chars at various temperatures



their relative proportions at the char surface. While surface properties may vary widely from particle to particle for a typical char batch, having an over-all picture of the elements that comprise a char surface can help elucidate how hydrogen sulfide might interact with each char. The EDS data (**Table 9**) on the virgin chars confirmed the variety of elements found through the elemental analysis for each char. The feces-derived chars had a diversity of minerals, including the alkali

earth metals Ca and Mg. These contribute to the high pH and thus the adsorption capacity of the fecal chars. As pyrolysis temperature increased, the relative proportions of all inorganic minerals

Table 9- SEM-EDS data showing the percent of elements by weight at the surface of various feces-derived chars

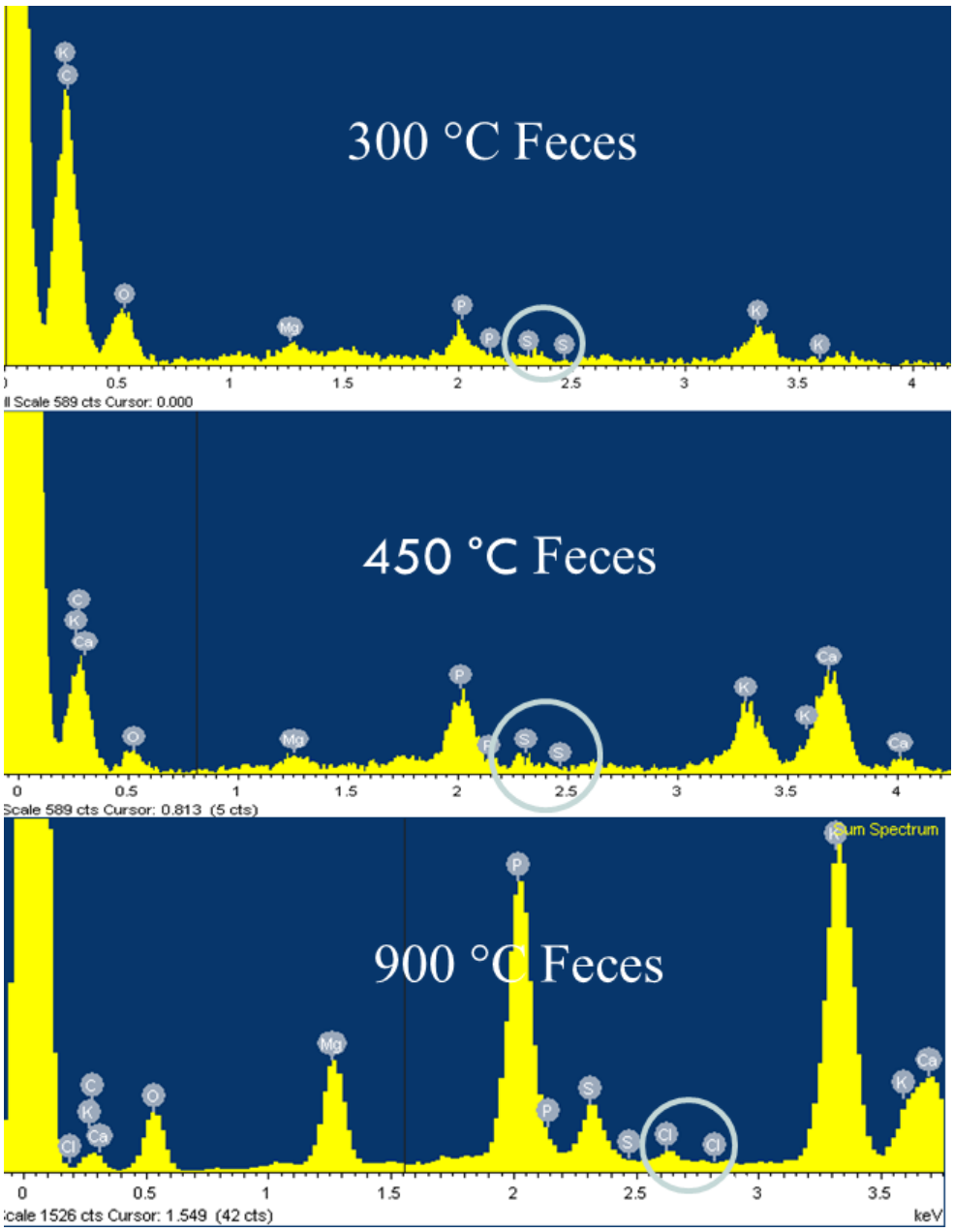
	300 °C Feces	**450°C Feces**	**900°C Feces**
Element	Wt%	Wt%	Wt%
C	77.37	61.17	37.36
O	18.65	15.83	26.41
Na	--	1.36	--
Mg	--	1.63	5.20
Si	--	1.11	--
P	0.96	5.57	10.92
Cl	--	1.43	--
K	1.85	8.36	8.36
Ca	1.17	3.53	11.74

increased at the surface. The presence of these metals at the surface surpasses expectations when compared to the results from the elemental analysis. This indicates that inorganic metals are concentrating at the surface during pyrolysis.

The SEM-EDS data also indicated the presence of sulfur at the surface of the exhausted feces-derived char that was not visible on virgin chars.

Figure 11 illustrates the distribution of elements on all chars following char exhaustion. The circles indicate the presence of sulfur, which was not found in the EDS surface data for any of the virgin chars, and is as shown for the feces-derived chars. (**Table 9**)

Figure 11-SEM-EDS data for exhausted chars showing the appearance of sulfur at the surface where previously it was not detected.


300 °C Feces
450 °C Feces
900 °C Feces
Scale 589 cts Cursor: 0.813 (5 cts)
cale 1526 cts Cursor: 1.549 (42 cts)
keV

PH

Surface pH plays a huge role in hydrogen sulfide adsorption and oxidation. Hydrogen sulfide is a week acid and is attracted to basic functional groups. More importantly, the presence of basic functional groups is thought to drive the dissociation onto a water film of Hydrogen sulfide into hydrogen and a hydrogen sulfide ion, a necessary step for H_2S oxidation. For effective dissociation, the pH of the char surface should be greater than the dissociation constant of hydrogen sulfide, which has primary and secondary dissociation constants of 7.2 and 13.9. A moderate pH will result in the preferential formation of sulfate as a result of the decrease in the concentration of elemental sulfur formed, allowing for complete oxidation to sulfate [32]. In the case of fecal char (**Table 10**), the surface pH of each char directly correlates with its breakthrough capacity. Interestingly, following char exhaustion, all of the chars remained basic, with the two higher temperature fecal chars strongly basic. This indicates that these chars still have some ability to catalyze the oxidation of hydrogen sulfide. Steady state breakthrough at a level that is a fraction

Table 10- pH before and after biochar exhaustion

	pH, virgin	**pH , exhausted**	Δ
300°C Feces	9.24	8.86	-.38
450°C Feces	10.63	10.45	-.18
900°C Feces	11.28	9.22	-2.06

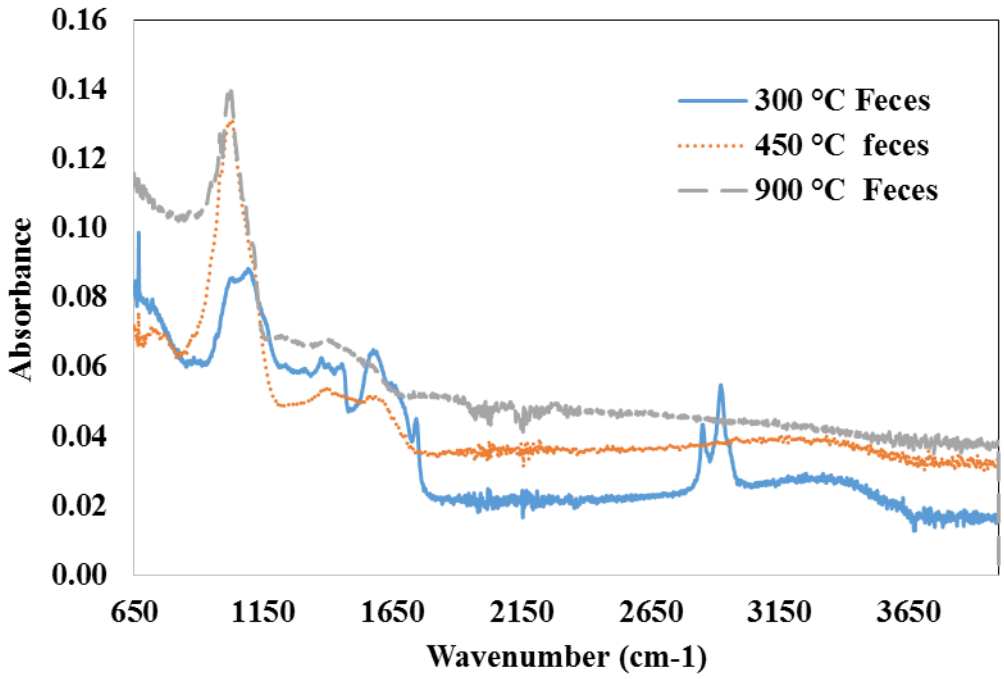
of the initial hydrogen sulfide concentration may have been the result of physical capacity being reached while catalysis continued on the char surface. It's also possible that longer breakthrough times associated with these chars resulted in the char drying and ultimately premature breakthrough. For the 450° C fecal char, the pH didn't change after exhaustion. This indicates that

the primary product on this char is elemental sulfur or precipitates such as $CaSO_4$. These are not acidic and do not result in a surface pH change.

FTIR

The fecal chars shown in **Figure 12** have an FTIR peak at (1430cm^{-1}), indicating the presence of carboxyl groups. The COO group is considered alkaline as it is de-protonated. The peak is strongest for the 300°C biochar, decreases for the 450°C fecal char, and is even smaller for the 900 °C fecal char. This is most likely due to the decomposition of the biomass structure at higher temperatures. A similar trend holds for aromatic C=C and C=O stretching at (1620cm^{-1})

Figure 12-Fourier Transform Ion Spectroscopy of fecal chars



and CH_2 stretching at (2920cm^{-1}), with this peak disappearing after 300 °C. On the contrary, Aluminum Silicates (1020cm^{-1}) increase with increasing pyrolysis temperature as a result of an increase in mineral content at higher temperatures. The presence of this peak aligns with the abundance of illite and

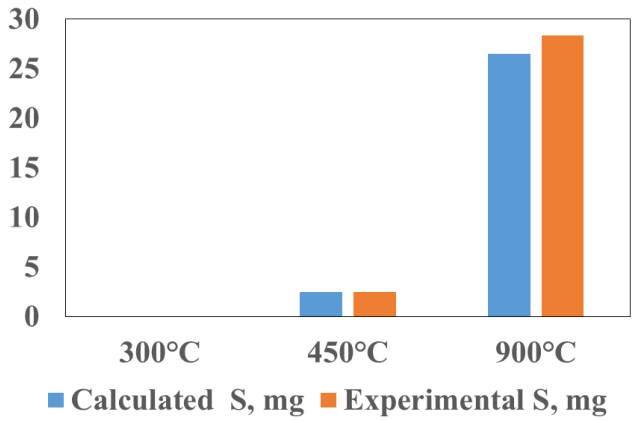
feldspar which have commonly been found in sewage sludge based biochars [42]. The FTIR data indicates that despite the disappearance of organic alkaline functional groups at higher temperatures, fecal char pH increases with increasing pyrolysis temperature as a result of the increase in the fraction of inorganic alkalinity.

Sulfur Speciation

Soluble sulfate concentration and sulfur mass balances both before and after char exhaustion were used to hypothesize the possible catalytic pathways for each biochar. Expected concentrations based on calculations and measured sulfur content for exhausted chars were used to verify the accuracy of analysis and make assumptions about the different sulfur species produced following adsorption of hydrogen sulfide onto fecal char. As shown in

Figure *13*, the calculated total sulfur and the measured total sulfur are relatively close. This indicates both that the analysis is fairly accurate and that the majority of sulfur remains sorbed to the char as elemental sulfur or soluble sulfate, and is not lost as SO_2.

Figure 13- Comparison of expected and measured sulfur content in exhausted chars: *Expected sulfur content calculated based on virgin char elemental analysis and breakthrough capacity; Experimental sulfur content calculated based on elemental and soluble sulfate analysis*

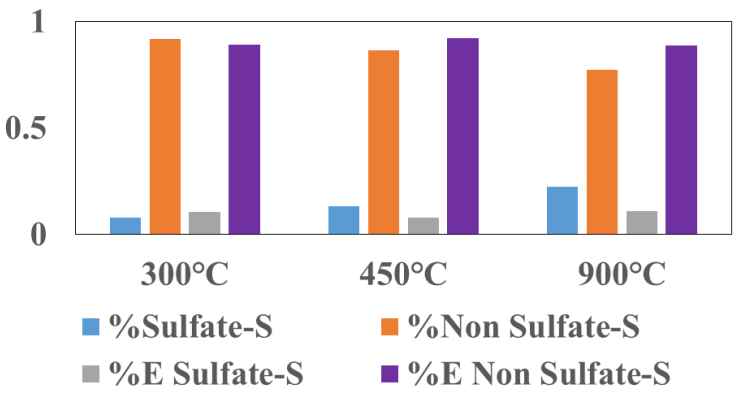


*Concentrations for 300 °C Char were too low to be significant

Based on the results as well as theories regarding traditional catalytic pathways for chars made from biomass with high inorganic content, sulfate and elemental sulfur seem to be the most

likely sulfur species produced. Complete oxidation to sulfate is the preferred pathway as it results in a water soluble byproduct that can be recovered, and allows for the regeneration of exhausted char. In the case of feces-derived char, complete oxidation of hydrogen sulfide to soluble sulfate seems to be a catalytic pathway, but sulfate is not the most readily formed byproduct. Ultimately, of the sulfur adsorbed/oxidized during the breakthrough experiments, 89% in the case of 900 °C char, 92% in the case of the 450 °C char, and 89% in the case of 300°C were present as sulfur species other than sulfate. This is in contrast to the relative proportions of non-sulfate sulfur species in virgin chars, which were 78%, 87%, and 92% for 900°C, 450°C, and 300°C fecal chars respectively. These values are visible in **Figure 14**.

Figure 14- Sulfur speciation to soluble sulfate or other forms of sulfur for sulfur adsorbed onto exhausted feces-derived char



*E - Exhausted

The results indicate that the complete oxidation of hydrogen sulfide to soluble sulfate is catalyzed at a similar rate irrespective of the surface area or pore volume. The consistent lack of significant conversion to sulfate across all temperatures may be a consequence of limited space. Xu et al. (2014) [42] speculated that micropores provide a space where elemental sulfur preferentially forms as a results of limited oxygen availability while sulfate, if it was formed, was

more likely to form on the surface. This signifies that sulfate should have made up a greater portion of the sulfur species in the lower temperature chars due to a lack of pore volume. However, pH and concentration also play a role. Poly-sulfides form at higher pH values due to the favorability of catalysis to elemental sulfur, the resultant increased S° concentration, and the subsequent interaction of S° with itself [32]. The pH for all three fecal chars was basic, with the pH being particularly high for both the 450 °C char and the 900°C char, leading to high concentrations of elemental sulfur. For all chars it appears that there is not sufficent room for dispersion and oxidation, and poly-sulfide will form more readily than sulfate.

4.3.3. Comparison to Wood Based Chars

In order to get a more objective gauge of the effectiveness of feces-derived biochar for the treatment of hydrogen sulfide, wood and bamboo based chars were tested under the same empirical conditions and characterized using the same analytical tools. The chars tested were 300 °C pine, 900 °C bamboo, and 1200 °C bamboo.

The static breakthrough tests showed that bamboo char was the highest performing of the wood and bamboo based chars. This is not unexpected as bamboo char has been tested and confirmed to be an effective hydrogen sulfide sorbent. Overall, the bamboo was the second most effective sorbent, following 900 °C feces-derived char, which had a breakthrough capacity that was approximately seven times more than bamboo char on a mass basis and four times more than bamboo on a volume basis. It should be noted that breakthrough for the bamboo char stabilized at 30 ppm, indicating that catalysis is occurring more efficiently on bamboo char. The normalized breakthrough capacities for the pine and bamboo chars are shown in **Table 11.**

Table 11-Breakthrough capacities for pine and bamboo based biochars, normalized by char mass and char volume

	Char Amount (g)	Water Amount (g)	Bulk Density (g/cm^3)	BT Capacity (mg/g)	BT Capacity (mg/cm^3)
300°C Pine	2.24	5	.18	.012	.002
900°C Bamboo	8.69	5	.70	4.97	3.503
1200°C Pine	1.54	5	.12	1.667	.708

*BT: breakthrough

BET data for the wood and bamboo chars was higher than for the feces-derived chars and was highest overall for the high temperature bamboo char. These chars still have surface area that is significantly lower than the 500 m^2 surface area of activated carbon (AC). On the other hand, pore volume is much more comparable between feces based chars and the pine and bamboo chars of equivalent temperature. Pore volume has been cited as a more important aspect of hydrogen sulfide adsorption than SA, making the expected breakthrough capacities based on BET less distinct. As discussed earlier, a distribution of micropores and mesopores is important for a chars H_2S breakthrough capacity. The 900 ºC bamboo char had the highest fraction of micropores of any char, followed by the 1200 ºC pine char, and then the 900 ºC fecal char. The lower temperature chars all had fairly negligible micropore volume and instead showed mostly mesopores with the distribution of macropores generally decreasing with increasing pyrolysis temperature. The micropore and mesopore distribution is best for the 900 ºC fecal char and the 1200 ºC bamboo char. The BET results for the pine and bamboo based chars are shown in **Table 12**.

Table 12 - BET surface area and pore volume data for bamboo and pine chars

	Surface Area (m^2/g)	Pore Volume (cc/g)	Micropore Volume Fraction	Mesopore Volume Fraction	Macropore Volume Fraction
300 °C Pine	0.7	0.001	0.07	0.67	0.26
900°C Bamboo	146	0.091	0.87	0.12	0.01
1200°C Pine	115	0.071	0.71	0.27	0.02

The elemental analysis for the pine and bamboo chars showed low inorganic mineral content for pine and bamboo chars relative to the feces-derived chars across the board. In general, the mineral content was negligible. Carbon content was higher for the wood and bamboo based chars than for the feces-derived chars with the relative percentage increasing with increasing temperature for the pine based chars. The amount of hydrogen decreased with increasing pyrolysis temperature, while the amount of nitrogen increased with increasing temperature. For nitrogen and carbon the trend was the opposite for feces-based chars. The elemental analysis for these wood based chars is shown in **Table 13**.

Table 13- Elemental analysis of pine and bamboo based chars

	Ca	K	Mg	S	Al	Cu	Fe	Mn	Zn	C	H	N
	wt%	wt%	wt%	wt%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	% C	%H	% N
300 Pine	0.17	0.09	0.033	<0.01	56	49	28	78.1	72.9	65.13	4.14	0.12
900 Bamb	0.05	0.11	0.023	<0.01	39	<5	72	1.85	238	88.21	0.74	0.29
1200 Pine	0.18	0.08	0.025	<0.01	57	<5	653	97.2	<3	87.95	0.18	0.33

The SEM-EDS data for the pine and bamboo char showed that the surface of these chars have been reduced almost exclusively to carbon at high temperatures, Oxygen is the only element

readily found at the surface, and it is only seen at the surface of the low temperature, 300 ºC, pine char. This is significantly different from the feces-derived char, which all have a variety of inorganic elements at the surface, with the fraction of these inorganics increasing at the surface with increasing pyrolysis temperature.

Table 14- Energy Dispersive Spectroscopy for pine and bamboo chars

	300°C Pine	**900°C Bamboo**	**1200°C Pine**
Element	Wt%	Wt%	Wt%
C	**76.64**	**>90**	**>90**
O	**23.36**	--	--

The pH values of the high temperature pine and bamboo based biochars are both basic and comparable to the 300 ºC feces-derived char. These chars all have pH values lower than the 450 ºC char, but not significantly below. The 900 ºC fecal char still has the highest pH of all at 11.28. The 300 ºC pine char has the only slightly acidic pH of any of the chars and also exhibited a negligible breakthrough capacity. The pH values of both the high temperature chars decreased significantly following char exhaustion. The bamboo char decreased the most of any of the chars. This is partly as a result of the fact that its breakthrough capacity was the seconds highest, and may also be partly explained by a higher conversion rate to sulfate. Sulfate is acidic and leads to decreased pH.

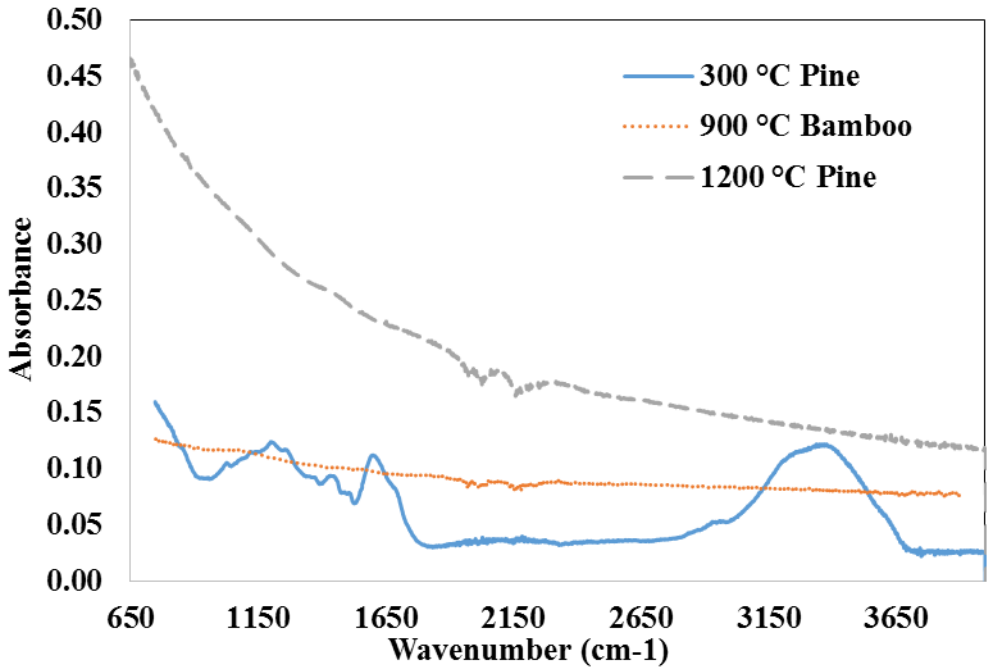
Table 15- pH values for pine and bamboo based chars before and after exhaustion

	pH, virgin	**pH , exhausted**	**Δ**
300°C Pine	6.11	6.31	+.2
900°C Bamboo	9.96	7.55	-2.41
1200°C Pine	9.59	7.93	-1.66

Based in FTIR analysis, the hydroxyl group, indicated by a broad band at 3320 cm^{-1}, was only visible on the 300 °C pine char and may account for the lower pH of this char. This char also had the C=C and C=O stretching as part of the aromatic ring peak at 1620cm^{-1}. The peak at 1430cm^{-1} correlates to carbonate.

A lack of peaks associated with high temperature pine and bamboo-based biochars correlates with the expected graphitic nature of these chars. At elevated temperatures, losses in hydrogen and oxygen content occur as a result of the cleavage and cracking of weak bonds within the biochar structure [87]. These data align with the elemental analysis already collected and serve as a contrast to the FTIR for the feces-derived chars. The FTIR analysis is shown in **Figure 15**.

Figure 15- Fourier Transform Ion Spectroscopy of pine and bamboo based chars



4.4. Conclusions

The results from these studies indicate that human feces-derived biochar can be transformed into an effective adsorbent for the toxic and malodorous gas, hydrogen sulfide. In literature, the performance of sewage sludge based chars has been associated with the presence of dispersed inorganic minerals and catalytic metals such as Ca, Zn, Fe, and Cu [85, 86]. The same results hold true for human feces-derived biochar. Increasing inorganic content results in increased alkalinity, creating optimal surface conditions for the formation of HS^- and H^+ and ultimately the formation of elemental sulfur and sulfate. The increase in inorganic content at higher pyrolysis temperatures results in higher breakthrough capacities. Across temperatures for feces-derived chars there is a consistent preference for non-sulfate production, most likely poly-sulfides or elemental sulfur species, of approximately 90%. The remaining 10% is fully oxidized to soluble sulfate.

When comparing feces- derived biochar to wood and bamboo based biochars, it was found that high temperature biochars, 900°C, outperformed low temperature biochars. It was also found that feces-derived biochar had higher breakthrough capacities than wood and bamboo based biochars. Based on the comparable pore volume and higher surface area in pine and bamboo based chars the wood char data supports the hypothesis that high breakthrough capacity for high temperature feces-derived chars is a result of higher inorganic content leading to high pH and a more favorable environment for hydrogen sulfide oxidation.

Though this research did not address the formation of a biofilm on the char surfaces during these static breakthrough tests, the experimental conditions, specifically the high humidity, make biological metabolism a very possible contributor to hydrogen sulfide oxidation. The long term capacity of any carbon based adsorbent would be highly impacted by biofilm formation. Biofilm

would likely greatly increase capacity, but may also result in pressure buildup due to filter biofouling.

The capacity for biofilm formation on adsorbent material has interesting applications for the treatment of the complex mixture associated with fecal pyrolysis exhaust. However, as discussed earlier, biofilter media with intrinsic buffering capacity and dispersed sulfur oxidizing bacteria may offer a more efficient alternative.

5. Odor and Hydrogen Sulfide Treatment: Biofiltration

Biofiltration represents a promising odor treatment technology for the complex gas mixture associated with fecal pyrolysis exhaust. This portion of the research focuses on understanding the feasibility and challenges associated with using biofiltration and is based on a comprehensive literature review and preliminary studies. The preliminary experiment involved the design and manufacture of a pilot scale biofilter and its short term use. While the long term experiments necessary to prove the effectiveness of biofiltration for exhaust treatment were not possible, this chapter does provide detailed information for the monitoring and evaluation of a biofilter and recommendations for design modifications.

5.1. Methods

5.1.1. Biofilter Design

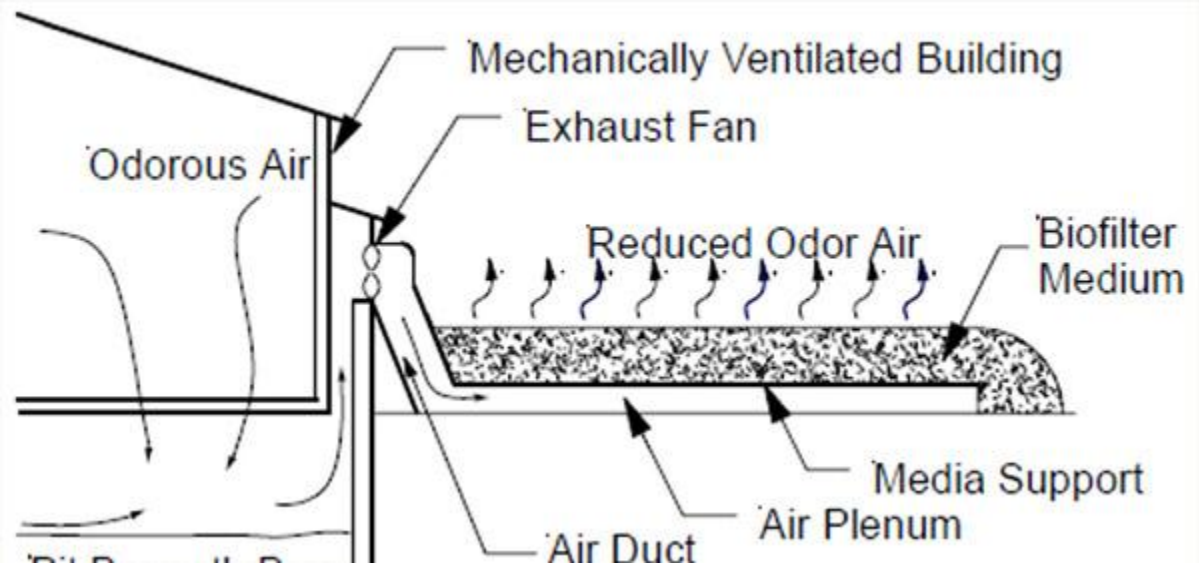
In order to explore the ability of a biofilter to handle the complex gas mixture emitted from the Sol-Char toilet, a pilot biofilter designed for a single user was created. The exhaust gas was produced inside of a one liter stainless steel reactor and pyrolysis was induced using band heaters. The resultant pyrolysis gases were then piped to the biofilter via stainless steel and aluminum tubing via a fiberglass fan.

The design of this biofilter was based on standard schemes for treating odors from a dairy livestock building. This project was based on the approximate calculated flow rate of 1.73 L/min, or .061cfm of the pyrolysis exhaust at 450 ºC. The exhaust from fecal pyrolysis will have a higher concentration of odorous compounds such as hydrogen sulfide that will peak only once a day, but will produce less of these compounds overall than a livestock building. This makes the addition of biochar, feces-derived or other, crucial for the effective long-term function of the biofilter. However, for the purposes of this initial pilot project, it was important to assess the ability of

microbes to metabolize the exhaust gases from fecal pyrolysis on their own, and biochar was not added.

The biofilter was built inside of plastic container with a volume of 2.31 ft^3. The depth was .91 ft. while the surface area on top and bottom was 2.52 ft^2. Flexible aluminum tubing connected to the pyrolysis reactor was bent to cover the bottom of the biofilter container and was perforated with one cm diameter holes one inch apart throughout. The tubing was then covered with gravel in order to ensure adequate mixing and even dispersion of the exhaust throughout the biofilter. A diagram of the basic biofilter layout for a dairy is show in **Figure 16**. The media support is gravel in the case of the pilot biofilter and it is combined with the air plenum.

Figure 16- A schematic showing the components of a typical biofilter taken from the University of Minnesota [88]

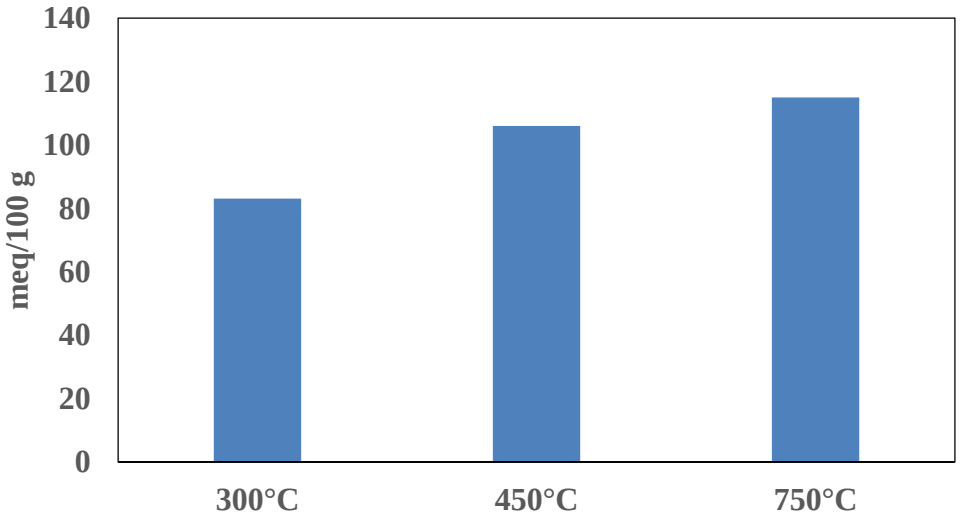


The biofilter material used was a combination of regular topsoil, organic topsoil made from mushroom compost and woodchips. The mushroom compost topsoil was added to increase the

microbial activity of the soil and made up approximately 25% of the total biofilter media. The wood chips helped increase the porosity, decreasing negative pressure and were added to the filter media until it tested above 40% porosity. The wood chips made up approximately 15% of the volume of the filter media.

In future studies, biochar can also be added to help buffer the soil in the case that it becomes too acidic. Based on data collected by part of the Sol-Char toilet project, the cation exchange capacity of soil increases when supplemented with fecal char. Cation exchange capacity (CEC) is defined as the number of exchangeable cations per dry weight that a soil is capable of holding. It's measured in millequivalents per 100 grams of soil (meq/100g) and increasing CEC is associated with higher soil fertility. As shown in **Figure 17,** the CEC increases when supplemented with chars pyrolyzed at higher temperatures. Closely related and of importance for the biofilter is base saturation. Base saturation is the number of exchangeable cations that are base cations such as Ca, Mg, and K. As the amount of exchangeable base cations increases, the ability to neutralize more acidity in a short amount of time increases. Based on the large amount of base cations in

Figure 17- Cation exchange capacity for soils supplemented with feces-derived biochar



fecal char, supplementing the biofilter with it may offer a very simple mechanism for preventing acidification of the soil.

The biofilter dimensions were decided based on a minimum empty bed contact time (EBCT) of 10 seconds. This number is a predication based on the metabolic activity expected to be present in a soil biofilter and previously built biofilters and should be as high as possible to ensure metabolism of all exhaust compounds [89]. EBCT is determined by dividing the empty reactor volume by the airflow rate. Thus, based on the volume of the bed, and a desired EBCT of 10 seconds, the maximum air flow rate can be 13.86 ft^3/s. Empty bed contact time and airflow rate are also related to pressure drop and media porosity. For a soil based biofilter, a porosity of greater than 40% voids is recommended to avoid excessive pressure drop. Media permeability should remain above this even after media compaction. Negative pressure drop was designed to be below 1.0 inch of water. **Equation 3** includes the equations used to design the biofilter based on the size, EBCT, porosity, and pressure drop requirements mentioned. Based on these equations, the design specifications in **Table 16** were chosen for the pilot biofilter.

Equation 3-Equations for calculating unit pressure drop and unit airflow rate based on volume and EBCT taken from the University of Minnesota [88]

$$V = media\ volume\ (ft^3)$$
$$D = media\ depth\ (ft)$$
$$A = media\ area\ (ft^2)$$
$$EBCT = empty\ bed\ contact\ time\ (s)$$
$$Q = airflow\ rate\ \left(\frac{ft^3}{\min}\right) = \frac{V}{EBCT} * 60\left(\frac{s}{\min}\right)$$
$$UAR = Unit\ airflow\ rate\left(\frac{ft^3}{ft^2 * S}\right) = \frac{Q}{A}$$
$$UPD = Unit\ presure\ drop\left(\frac{H_2O}{ft}\right)$$
$$UPD = 8.82 * 10^{11} * (percent\ voids)^{-8.6} * Unit\ airflow\ rate^{1.27}$$
$$TPD = Total\ presure\ drop\left(\frac{H_2O}{ft^2}\right) = \frac{UPD}{D}$$

Table 16- Biofilter parameters

Porosity (%)	V (ft^3)	EBCT (s)	UAR ($ft^3/ft^2/s$)	Q (ft^3/s)	UPD (H_2O/ft.)	TPD (H_2O/ft^2)
40	2.31	9.99	5.5	13.86	0.12	.13

5.1.2. Reactor Tests

Reactor tests were run between 3 and 5 days a week for 1 month. This schedule was designed to emulate the intermittent release of exhaust from the Sol-Char toilet based on the unpredictable nature of weather. A biofilter for the Sol-Char toilet would need to be able to withstand feast and famine, alike. For each test 0.75 liters of fecal waste was placed in the reactor and heated up to 400 °C using band heaters. The reactor was kept at this temperature for 2 hours to ensure complete pyrolysis of the waste. The airflow rate was set at 13.3 ft^3/s by adjusting the voltage applied to the attached fan. The biofilter was kept moist throughout via the application of water evenly over the top every other day.

5.1.3. Hydrogen Sulfide & Odor Quantification

Hydrogen sulfide measurements were taken using a GasAlertMicro5IR chemical sensor. The sensor was placed above the biofilter and was also periodically moved to various locations outside of the reactor to ensure that hydrogen sulfide wasn't escaping from any other part of the reactor. In order to quantify the approximate amount of hydrogen sulfide released during each reactor test, the same GasAlertMicro5IR hydrogen sulfide chemical sensor was used. A pump with tubing for extended reach was attached to the sensor and it was piped into the exhaust tube directly above the reactor. Observations of the ambient odor were recorded throughout each reactor experiment.

5.1.4. Media Characterization Tests

Various system parameters can be used to determine the effectiveness of a long term pilot biofilter. While these tests could not be completed for this thesis, future tests would benefit from

constant monitoring. Important system parameter for biofilter health as well as an analytical technique that can be used to monitor each are discussed below. More detailed protocol information can be found in Appendix III.

Microbial Biomass

The chloroform fumigation direct extraction protocol can be used to assess the soil microbial biomass carbon in a biofilter before and after exposure to hydrogen sulfide. As the biofilter ripens, you would expect the biomass to increase or at least remain constant. This test can this be used to ensure biofilter health. For this test, the difference between carbon in the fumigated and non-fumigated samples is the chloroform-labile C pool (EC) and is proportional to the microbial biomass carbon as indicated in **Equation 4**. The proportionality constant, kEC, is soil specific, but can be estimated at .45 based on previous studies. The protocol for this was created by Vance et al. (1987) [90].

Equation 4- Microbial biomass carbon

$$C = EC/kEC$$

Results from this test provide valuable information regarding the initial biomass present in the soil biofilter, and also show how microbes are affected as a biofilter continues to be used. A healthy biofilter is expected to have large amounts of microbial biomass carbon. A decrease in biomass following biofilter use would indicate that the conditions are not appropriate for microbial growth.

Sulfur Oxidizing Bacteria

Because of the importance of the sulfur cycle, sulfur oxidizing bacteria are essentially ubiquitous in soils. Hydrogen sulfide is soluble in both oil and water, and thus partitions into moist soils and water [91]. Hydrogen sulfide is thought to adsorb onto clay and organic matter due to

this solubility [92]. Several species of heterotrophic microbes in soil and water oxidize hydrogen sulfide to elemental sulfur, with half-lives ranging from one to several hours [92]. A warm damp environmental such as a biofilter for exhaust gases is likely to contain autotrophic bacteria that oxidizes hydrogen sulfide to sulfate [93]. To confirm the presence of the autotrophic sulfur oxidizing bacteria and provide a most probable number (MPN), bacterial cultures can be grown based on recipes for the autotrophic sulfur oxidizing bacteria *Thiobacillus*. *Thiobacillus* can metabolize a wide variety of sulfur compounds at multiple pH values, including hydrogen sulfide. There are a variety of other recipes that can also function for this purpose. The presence of different types of oxidizing bacteria can be confirmed by changing the broth recipe and incubating with hydrogen sulfide gas.

The *Thiobacillus* broth can be made using the recipe in **Table 17**. This recipe is a modification of the original *Thiobacillus* recipe created by Starkey (1935) by HIMEDIA labs [94]. These cultures can be grown at multiple pH values to select for hydrogen sulfide oxidizing bacteria that function at different soil pH values using sodium hydroxide and hydrochloric acid. The presence of sulfur oxidizing bacteria should be confirmed every month.

Table 17 - *Thiobacillus* broth and agar ingredients

Ingredients	**Grams / Liter**
Ammonium sulphate	0.400
Monopotassium phosphate	4.000
Calcium chloride	0.250
Ferrous sulphate	0.010
Magnesium sulphate	0.500
Sodium thiosulphate	5.000
***Agar**	12.500

*do not add agar for the broth

Porosity

Measuring the porosity of a biofilter is important to ensure that there isn't a buildup of negative pressure. Over time, biofilters tend to compact as a result of their own weight. Ensuring that porosity remains above 40% is crucial to maintaining a strong biofilter. Measurements should be made weekly and samples should be taken so that the soil is as undisturbed as possible before testing. The method for determining porosity is simple and only requires a known volume of soil and a known volume of water. Water is pored over the soil until the soil is saturated. The amount of water used to fill the soil is equivalent to the pore space while the total volume is equal to the total volume of the soil sample. To calculate the % pore space use **Equation 5**.

Equation 5 – Equation for calculating porosity

$$\%\ pore\ space = \frac{pore\ space}{total\ volume} * 100$$

Moisture

Soil moisture needs to be maintained in order to ensure a healthy environment for microbial growth. For a healthy soil biofilter, moisture content should be maintained around 20%. This level should be confirmed randomly throughout the operation of the biofilter. It is also important that soil samples for measurement be taken at various depths.

Soil moisture content is equivalent to the ratio of the mass of water present to the dry weight of the soil sample. It can also be expressed by volume as a ratio of water to the total volume of the soil sample. The gravimetric method can be used in this case to determine the moisture content. The calculation for moisture content on a dry weight basis can calculated with the formula below in **Equation 6** [95].

Equation 6-Calculation for moisture content on a dry weight basis

$$\theta_d = \frac{(wt\ of\ wet\ soil + tare) - (wt\ of\ dry\ soil + tare)}{(wt\ of\ dry\ soil + tare) - (tare)}$$

pH

Soil pH is an important variable as it controls the chemical processes that occur. It affects plant nutrient accessibility by regulating the chemical forms of nutrients such as sulfur. The ideal pH range for soil is between 5.5 and 7.0.

Metabolized hydrogen sulfide may affect the pH of the soil biofilter through the formation of iron sulphates and aluminum sulphate or by the oxidation of elemental sulfur (S°) to sulfuric acid. Buffering capacity of soils is a function of a soils cation exchange capacity, which is determined by the clay content of the soil, the type of clay and the amount of organic matter present [96]. The pH of the biofilter should be regularly monitored using a standard laboratory pH.

5.2. Results & Discussion

5.2.1. Hydrogen Sulfide & Odor Quantification

The release of hydrogen sulfide before treatment was monitored during two of the reactor tests. The peak release of hydrogen sulfide for these two tests was 31 and 37 respectively. This aligns with what is expected based on the characterizations of hydrogen sulfide and odor explained earlier. However, it is possible that these numbers are higher than they should be because of increased negative pressure causing exhaust to back up. Negative pressure is expected to increase with age as the biofilter becomes more compact.

Overall, the reactor test was run 13 times. Hydrogen sulfide was never detected above the biofilter or in any of the locations where a leak was detected. The chemical sensor has a sensitivity of 1 ppm. Microbial metabolism inside of the biofilter in combination with the immediate

dispersion of hydrogen sulfide when it reaches the outdoors explain the effectiveness of treatment for this dangerous and odorous gas and a lack of detection where leaks were confirmed.

However, odor, while improved, continued to be an issue. The exhaust from the pyrolysis of human feces has an intense smell, comparable to the smell of burning macaroni and cheese. More specifically, the aroma is extremely pungent, sharp, a little rancid and lingers on anything it comes into contact with. Immediate dilution on a windy day by the atmosphere is not sufficient to make the odor tolerable. Based on observations, exhaust treated by the biofilter was significantly less potent. This may be because the release of odor seemed to be more intermittent and primarily via leaks in the pipes conducting the exhaust to the biofilter. The smell occurs after drying has finished and while pyrolysis is taking place. The smell seemed to be the strongest just before the highest heating temperature of 400 ºC was reached. This aligns with data discussed in chapter 3 of this thesis, regarding when the most intense release of hydrogen sulfide occurs.

As the biofilter ripened and more reactor tests were performed, the smell associated with the leaks increased. Intuitively, you would expect biofilter acclimation to result in better treatment performance. This suggests that compaction of the biofilter was resulting in an increase in negative pressure. The buildup most likely resulted in the escape of the exhaust through small leaks that previously offered more resistance than the path through the biofilter. In addition, there was a large buildup of tar in the pipes. This may have contributed to the increased odor associated with the reactor.

One of the most positive outcomes from the biofilter was the elimination of the exhaust plume. Fecal pyrolysis exhaust without treatment is visible as a greyish tan plume. The visibility of the plume is most likely the result of high particle content associated with the combustion of materials with a high ash content as well as the moisture present in the fecal samples.

5.2.2. Challenges & Future Work

If the biofilter is expected to work long term, then design modifications are necessary. The porosity of 40% that was designed for was not sufficient to prevent a negative pressure buildup. In order to increase porosity, wood, and more naturally porous material such as compost should be mixed in with the soil biofilter. Adding compost to the biofilter has the added benefit of increasing the biomass of the biofilter. In addition, a larger size that provides more of a buffer in instances where excessive hydrogen sulfide might be released is recommended.

An added concern that must be addressed is what should be done with leachate inside of the exhaust pipes connecting the pyrolysis reactor to the biofilter. The buildup of leachate may affect the performance of the odor module, would contribute to odor, and would decreases the overall lifetime of the exhaust pipes. Microbial degradation of the leachate or high temperature oxidation of the leachate are both potential treatments. Challenges facing microbial degradation include creating and maintaining a stable environment for their growth. Challenges associated with oxidation include finding a way to reach sufficiently high temperatures in the exhaust pipes, and also finding a way to isolate this high heat environment from the biofilter, which should be maintained at temperatures below 50 °C.

The use of a biofilter for pyrolysis treatment becomes more feasible if biochar is used as a soil amendment. Biochar offers a potential mechanism for retaining hydrogen sulfide in soils until it can be metabolized by microorganisms. In particular, a lack of sufficient microbial activity for metabolizing hydrogen sulfide has been a huge limitation for soil based biofilters. As discussed in chapter three of this thesis, combining biofiltration with adsorption has been shown to be successful. In particular, based on the results of the adsorption studies, it looks like feces-derived

biochar may serve as a promising soil amendment. The basic pH and CEC may serve to counteract the acidification of soils caused by the influx of sulfur into the soil and the sulfur cycle.

Ensuring exhaust temperature is appropriate for microbial growth is another important challenge. Microbes can be extremely temperature sensitive. Based on Arrhenius Law, inside a narrow range, the rates of chemical reactions and biological processes double for every temperature increase of 10 degrees. Thus, soil temperature directs the rates and directions of reactions and the speed of metabolism in a soil biofilter. It has been shown that communities can perform better over time in response to increased temperatures up to 50 ºC [97]. Measurements on the exhaust during the odor and hydrogen sulfide quantification studies indicated that the exhaust temperature is unlikely to exceed 37.8 ºC, or 100 ºF. Thus, it seems that the metabolism of microbes in the biofilter may be enhanced when exposed to fecal exhaust. However, less is known about how intermittent exposure to higher temperatures will impact the long term efficiency of the biofilter. Studies examining these dynamics should be undertaken.

6. Scalability of Odor Treatment Options

The above studies indicate that adsorption of hydrogen sulfide and biofiltration of fecal pyrolysis exhaust have a lot of potential as odor treatment options for fecal pyrolysis exhaust. To better understand the practicality of using these treatments, the feasibility of scaling each option up are analyzed below.

6.1. Adsorption

The calculations described below were used to determine the amount of fecal char required to treat fecal pyrolysis exhaust for a family of four for one year. The calculated adsorption capacity of 900 °C fecal char was 15.7 mg/cm^3 for a gas stream with 90 ppm hydrogen sulfide at a flow rate of 200 sccm. For simplicities sake, the highest hydrogen sulfide release recorded during the fecal pyrolysis hydrogen sulfide quantification studies, 90 ppm, was used to calculate the total release of hydrogen sulfide from the pyrolysis of a family's fecal waste during one year. The amount of hydrogen sulfide released was calculated to be approximately .0366 g for one experiment in chapter 2 of this thesis. This amount is very conservative and assumes the highest amount of hydrogen sulfide release that could be observed for fecal pyrolysis at a lower highest heating rate. Those studies utilized two stool samples. A family of four was assumed to produce 1.5 samples every day for this scale up, resulting in a release of hydrogen sulfide that is approximately 3 times larger than the recorded hydrogen sulfide release for 2 stool samples daily. The numbers used for scaling up treatment for one year for a family of four are below in **Table 18**.

Table 18- Values for the treatment of hydrogen sulfide from fecal pyrolysis exhaust for a family of four for one year

Daily H_2S (g)	Annual H_2S (g)	Char BT Capacity (g/m^3)	Char volume for annual treatment (m^3)
0.11	40.08	15.97	2.51

The results indicate that a significant volume of high temperature feces-derived char is required to adsorb the annual amount of hydrogen sulfide released from the pyrolysis of feces from a family of four. Finding space for a 2.51 m^3 adsorption filter would be particularly challenging in an urban environment. The breakthrough capacity of high temperature fecal char is comparable to chars that can sufficiently treat gas streams with low concentrations of hydrogen sulfide for long periods of time. However, it may not be able to effectively treat fecal pyrolysis exhaust for long periods of time due to the high concentration of hydrogen sulfide and resultant high volume of adsorption material required for treatment. To ensure adequate long term treatment of fecal pyrolysis exhaust, either a smaller volume of char must be used and replaced frequently, or adsorption must be supplemented with biofiltration to elongate the lifespan of the fecal char. However, replacing fecal char often is a very viable option based on fecal char availability. A four person home could produce up to 51.1 m^3 of fecal biochar based on a conservative yield of 5% and a daily output of 350g of feces per person. That is enough char to treat twenty times the amount of hydrogen sulfide produced annually in a four person home.

6.2. Biofiltration

The following calculations assume that leaks detected during reactor tests are a result of negative pressure build up as well as a lack of an airtight exhaust transport system, rather than a lack of metabolic capacity or sufficient EBCT in the biofilter itself. The pilot biofilter was designed

to treat one stool sample 3-4 times a week. In order to scale the biofilter up to treat exhaust from a family of four, the biofilter would have to be approximately 8 times larger, or large enough to treat 8 samples daily. This increases the volume necessary from 2.31 $ft.^3$ to 18.5 $ft.^3$ or .52 m^3. This large amount of space may not be available in the urban environment. Optimally, the biofilter would be designed as part of a garden or would be located above or below the toilet to maximize the efficiency of the space used. As large as the space sounds, it is also important to remember that the biofilter can be built underground, saving space, and lowering the risk for exhaust leaks. If the depth of the biofilter is 1.5 ft., than a surface area of 3 by 4 ft. or 6 by 2 ft. would be all that was required. Using the soil from the biofilter to grow plants has the added benefit of providing a built in indicator of soil health. Another option to decrease biofilter size would be to increase the metabolic activity on the soil. This could be done via the addition of more compost, which is more microbially active. Supplementing the biofilter with fecal char will similarly decrease the necessary biofilter footprint. The larger the proportion of char, the less restrictive the EBCT. The char serves to hold the hydrogen sulfide in place until it can be metabolized and has the added benefit of catalyzing the oxidation of hydrogen sulfide itself. The presence of a large community of microorganisms may also serve to process any adsorbed elemental sulfur, extending the adsorptive lifetime of the char.

7. Conclusions

7.1. Odor Characterization

Fecal pyrolysis exhaust was found to have a strong odor at 510,000 odor units when collected with a hydrogen sulfide concentration of 32 ppm. That odor concentration puts its strength somewhere between industrial exhaust and anaerobic digestion gas. Hydrogen sulfide is one of the lowest threshold odor compounds as well as one of the most dangerous compounds released during the fecal pyrolysis process. The majority of hydrogen sulfide is released after char drying and before the internal char temperature has reached its highest heating temperature.

The shifting of hydrogen sulfide peaks to higher temperatures as the peak pyrolysis temperature increases indicates that higher temperatures result in the release of hydrogen sulfide that isn't released at lower temperatures. This is not unexpected as pyrolysis gas makes up a larger proportion of pyrolysis byproducts at higher heating temperatures. Rough estimates of the total hydrogen sulfide released during fecal pyrolysis at different temperatures align with this hypothesis and also fit within the range of expected hydrogen sulfide levels in fecal samples.

7.2. Odor Treatment

High temperature fecal biochar proved to be an effective adsorbent for hydrogen sulfide. The breakthrough capacity calculated after static testing was comparable to sewage sludge based adsorbents and wood based biochars. However, the 900 ºC fecal char in this study outperformed high temperature bamboo char and wood char, which both had lower than expected breakthrough capacities, by over a factor of 10. This indicates that under more optimal experimental conditions, fecal biochar may perform even better. The most probable reason for the high performance of 900 ºC fecal char was the presence of alkali earth metals, and an extremely high pH that encourages the formation of HS^-, leading ultimately to the oxidation of hydrogen sulfide. High temperature

fecal biochar is an exciting potential adsorbent for hydrogen sulfide in exhaust streams, but its lower capacity means that excessive volumes of fecal char are required to treat the exhaust long term. In addition, due to rapid fouling, it is unlikely to effectively treat the complex matrix of compounds associated with exhaust odor over a long period.

Based on preliminary studies and an extensive literature review, a soil based biofilter supplemented with fecal biochar represents an elegant prospective solution for sustainably treating complex exhaust streams such as the one produced by the Sol-Char toilet. It is particularly applicable in the developing world where replacement parts must be available locally and limited maintenance is desired. Further research could lead to a mature odor treatment module that closes the resource loop, enhances the Sol-Char toilet through both odor treatment and improved aesthetics, and has the potential to be used for the treatment of exhaust and odor from numerous sources. The Reinvent the Toilet Challenge is currently exploring many combustion and heat based toilet technologies. Loughborough University and its toilet based on the hydrothermal carbonization of fecal sludge, and Climate Foundation et al. and their toilet based on pyrolysis are just a couple examples of technologies where adsorption and biofiltration may be applicable.

7.3. Future Work

7.3.1. Odor and Hydrogen Sulfide Quantification

- Further research needs to be done to verify the calculated H_2S concentration associated with fecal pyrolysis exhaust.
- A larger odor panel should be used to characterize the odor from fecal pyrolysis exhaust.
- A wider range of pyrolysis temperatures and ramp rates should be tested to further characterize the release of hydrogen sulfide

- The flow rate should be further characterized in order to more accurately calculate the total hydrogen sulfide release during fecal pyrolysis.

7.3.2 Adsorption of Hydrogen Sulfide with Feces-Derived Char

- Breakthrough capacity should be calculated using standard dynamic breakthrough tests.
- Different humidity levels should be tested to see the impact on fecal-char capacity.
- Thermal analysis should be performed
- Moisture content and water holding capacity should be examined for their effects on char capacity
- The presence of microbial activity, if confirmed, should be explored for its effect breakthrough capacity
- X-Ray fluorescence spectra and X-Ray diffraction patterns should be obtained to better characterize the surface of fecal char. This will provide a better understanding of the likely mechanism of catalysis.

7.3.3. Biofiltration

- Design adjustments and further studies to assess the long term efficacy of the biofilter for the purpose of treating fecal pyrolysis exhaust are needed.
- Two long term pilot tests should be run to test the long term effectiveness of a soil biofilter on its own and a soil biofilter supplemented with fecal char.
- The system parameters should be monitored long term to identify how they are affected by exposure to fecal pyrolysis exhaust.
- A mechanism for dealing with pyrolysis tars should be designed

References

[1] W.H. Organization, *Progress on Sanitation and Drinking-Water: 2013 Update*, 2013, pp. 40.

[2] F.B.M. Gates, *Water, Sanitation & Hygiene: Strategy Overview*, in *GatesFoundation.org*, 2014.

[3] J. Sim, *The world toilet crisis can be solved*, in *The Economist*, Analysis & Opinions, 2014.

[4] D. Laird, P. Fleming, B. Wang, R. Horton, and D. Karlen, *Biochar impact on nutrient leaching from a Midwestern agricultural soil*, in *Geoderma*, 2010, pp. 436-442.

[5] M.K. Hossain, V. Strezov, K.Y. Chan, A. Ziolkowski, and P.F. Nelson, *Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar*, in *Journal of Environmental Management*, 2011, pp. 223-228.

[6] J.L. Moore JG, Osborne DN, *Gas-Chromatographic and Mass-Spectrometric Analysis of the Odor of Human Feces*, in *Gastroenterology*, 1987, pp. 93: 1321-1329.

[7] G. Leonardos, D. Kendall, and N. Barnard, *Odor threshold determinations of 53 odorant chemicals*, in *Journal of the Air Pollution Control Association*, 1969, pp. 91-95.

[8] S. Yaman, *Pyrolysis of biomass to produce fuels and chemical feedstocks*, in *Energy conversion and management*, 2004, pp. 651-671.

[9] A. Demirbas, *Effect of temperature on pyrolysis products from biomass*, in *Energy Sources 29*, 2007, pp. 4: 3290336.

[10] K. Cantrell, *Impact of pyrolysis temperatures and maure source o physiochemical characteristics of biochar*, in *Bioresource Technology*, 2012, pp. 107: 419-438.

[11] R.B. DA Laird, JE Amonette, J Lehmann, *Review of the pyrolysis platform for coproducing bio-oil and biochar*, in *Biofuels, Bioproducts and Biorefining 3*, 2009, pp. 5: 547-562.

[12] D. Day, R.J. Evans, J.W. Lee, and D. Reicosky, *Economical CO2, SOx, and NOx capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration*, in *Energy-the International Journal*, 2005, pp. 2558-2579.

[13] B.J. Ward, T.W. Yacob, and L.D. Montoya, *Evaluation of Solid Fuel Char Briquettes from Human Waste*, in *Environmental science & technology*, 2014, pp. 9852-9858.

[14] J. Lehmann, *A handful of carbon*, in *Nature*, 2007, pp. 143-144.

[15] IBI, *Frequently Asked Questions*, in *International Biochar Initiative*, 2013.

[16] T. Yacob, R. Fisher, R. Mahoney, J. Kearns, B. Ward, S. Summers, K. Linden, and A. Weimer, *Fecal sludge treatment by pyrolysis: characterization of exhaust gas and odor*

treatment, in *UNC Water and Health Conference*, University of North Carolina, Chapel Hill, 2013.

[17] A. Tangerman, *Measurement and biological significance of the volatile sulfur compounds hydrogen sulfide, methanethiol and dimethyl sulfide in various biological matrices*, in *Journal of Chromotography B*, 2009, pp. 877: 3366-3377.

[18] M. Koe L, ASCE, Tan N, *Field Performance of ACtivated Carbon Adsorption for Sewage Air*, in *Journal of Environmental Engineering* 1990, pp. 116: 721-734.

[19] I.P.o.C. Safety, and W.H. Organization, *Hydrogen sulfide: human health aspects*, World Health Organization, 2003.

[20] L.O. Smet E, Van Lengenhove H, *Treatment of Waste Gases Contaminated with Odorous Sulfur Compounds*, in *Critical Reviews in Environmetental Science and Technology 28*, 2010, pp. 1: 89-117.

[21] O.S.a.H. Administration, *Safety and Health Topics: Hydrogen Sulfide*, United States Department of Labor, 2014.

[22] U.S.E.P. Agency, *Toxicological Review of Hydrogen Sulfide*, EPA ed., 2003.

[23] A. Van Harreveld, P. Heeres, and H. Harssema, *A review of 20 years of standardization of odor concentration measurement by dynamic olfactometry in Europe*, in *Journal of the Air & Waste Management Association*, 1999, pp. 705-715.

[24] A.C. Stern, *Air Pollution: The effects of air pollution*, Vol. 2, Elsevier, 1977.

[25] R.M. Heck, R.J. Farrauto, and S.T. Gulati, *Catalytic air pollution control: commercial technology*, John Wiley & Sons, 2012.

[26] E.S. Hill, *Process for recovering sulfur from fuel gases containing hydrogen sulfide, carbon dioxide, and carbonyl sulfide*, Google Patents, 1976.

[27] A.A. Bagreev, Kuangm, Wayne, Bandosz, Teresa J, *Predictions of H2S Breakthrough Capacity of ACtivated Carbon at Low Concentrations of Hydrogen Sulfide*, in *Adsorption*, 2005, pp. 11: 461-66.

[28] C.D. Cooper, and F. Alley, *Air pollution control: A design approach*, Vol. 2, Waveland Press Prospect Heights, IL, 1994.

[29] T. Bandosz, *Effect of Pore Structure and Surface Chemistry of Virgin Activated Carbons on Removal of Hydrogen Sulfide*, in *Carbon 37*, 1999, pp. 483-491.

[30] W. Feng, S. Kwon, E. Borguet, and R. Vidic, *Adsorption of Hydrogen Sulfide onto Activated Carbon Fibers: Effect of Pore Structure and Surface Chemistry*, in *Environmental Science & Technology*, American Chemical Society, 2005, pp. 9744-9749.

[31] M.C. A Dalai, M De, *Direct oxidation of Hydrogen sulfide to Sulphur Using Impregnated ACtivated Carbon Catalysts*, in *The Canadian Journal of Chemical Engineering*, 2008, pp. 86: 768-777.

[32] T.J. Bandosz, *On the Adsorption/Oxidation of Hydrogen Sulfide on Activated Carbons at Ambient Temperatures*, in *Journal of Colloid and Interface Science*, 2002, pp. 1-20.

[33] A. Bouzaza, A. Laplanche, and S. Marsteau, *Adsorption–oxidation of hydrogen sulfide on activated carbon fibers: effect of the composition and the relative humidity of the gas phase*, in *Chemosphere*, 2004, pp. 481-488.

[34] K. Hedden, L. Humber, and B. Rao, *VDI-Bericht 253 S. 37/42*, in *VDI-Verlag, Duesseldorf*, 1976.

[35] T.E.L. Ghosh T.K., *Kinetics and reaction mechanism of hydrogen sulfide oxidation over activated carbon in the temperature rance of 125-200 C*, in *Journal of Chemical Engineering*, 1986, pp. 64: 969-76.

[36] B.A.B.T. Adib F., in *Environmental Science and Technology*, 2000, pp. 34: 686.

[37] J.F.-T. Tsai Juin-Horng, Chiang Hung-Lung, *Removal of H2S from Exhaust Gas by Use of Alkaline Activated Carbon*, in *Adsorption*, 2001, pp. 7: 357-366.

[38] G. Shang, G. Shen, T. Wang, and Q. Chen, *Effectiveness and mechanisms of hydrogen sulfide adsorption by camphor-derived biochar*, in *Journal of the Air & Waste Management Association*, Taylor & Francis, 2012, pp. 873-879.

[39] G. Shang, G. Shen, L. Liu, Q. Chen, and Z. Xu, *Kinetics and mechanisms of hydrogen sulfide adsorption by biochars*, in *Bioresource Technology*, 2013, pp. 495-499.

[40] A. Ros, M.A. Montes-Moran, E. Fuente, D.M. Nevskaia, and M.J. Martin, *Dried Sludges and Sludge-Based Chars for H2S Removal at Low Temperature: Influence of Sewage Sludge Characteristics*, in *Environmental Science & Technology*, American Chemical Society, 2005, pp. 302-309.

[41] T.J. Bandosz, and K.A. Block, *Removal of Hydrogen Sulfide on Composite Sewage Sludge-Industrial Sludge-Based Adsorbents*, in *Industrial & Engineering Chemistry Research*, American Chemical Society, 2006, pp. 3666-3672.

[42] X. Xu, X. Cao, L. Zhao, and T. Sun, *Comparison of sewage sludge- and pig manure-derived biochars for hydrogen sulfide removal*, in *Chemosphere*, 2014, pp. 296-303.

[43] A.A. Chan, *Attempted biofiltration of reduced sulphur compounds from a pulp and paper mill in Northern Sweden*, in *Environmental progress*, 2006, pp. 152-160.

[44] A. Wani, Branion R, Lau A, *Biofiltration: A promising and cost-effective control technology for Odors, VOCs and air toxins* in *Jourrnal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology, 32*, 2008, pp. 7: 2027-2055.

[45] H. Bohn, *Soil and Compost Filters of Malodorant Gases*, in *Journal of the Air Pollution Control Association 25*, 2012, pp. 9: 953-955.

[46] R. Govind, *Biofiltration: An innovative technology for the future*, University of Cincinnati, Cincinnati.

[47] L.C. Carlson DA, *Soil bed for the control of sewage odors*, in *Water Pollution Control Federation Volume 38*, 1966, pp. 3: 829-840.

[48] B.H. Prokop WH, *Soil Bed System for Control of Rendering Plant Odors*, in *Journal of the Air Pollution Control Association, 35*, 1985, pp. 12: 1332-1338.

[49] C. Pedersen, *Function and structure of biofilters removing sulfur gasses*, Department of Bioscience, Aarhus University, 2012.

[50] B.J. Janzen HH, *Measurment of sulfur oxidation in soils*, in *Soil Science* 1987, pp. 143: 444-452.

[51] P.J. Edwards, *Sulfur Cycling, Retention, and Mobility in Soils: A Review*, United States Department of Agriculture, Radnor, Pensylvania, 1998.

[52] J.K. Nicolai RE, *Biofilter media mixture ratio of wood chips and compost treating swiine odors*, in *Water Science and Technology 44*, 2001, pp. 44: 261-267.

[53] J. Devinny, Deshusses MA, Webster TS, *Biofiltration for Air Pollution Control*, CRC Press, 1998.

[54] A.E. Yang Y, *Biofiltration Conntrol of Hydrogen Sulfide 1. Design and Operational Parameters*, in *Air & Waste 44*, 2012, pp. 7: 863-868.

[55] K. Janni, Nicolai R, Hoff S, Stenglein R, *Biofilter for Ofor and Air Pollution Mitigation in Animal Agriculture*, Air Quality Education in Animal Agriculture, USDA, 2011.

[56] Q.G. Estrada JM, Lebrero R, Munoz R, *Step-feed biofiltration: A low cost alternative configuration for off-gas treatment*, in *Water Research 47*, 2013, pp. 4312-4321.

[57] K.-L. Ho, Chung Y-C, Lin YH, Tseng C-P, *Microbial population analysis and field application of biofilter for the removal of volatile-sulfer compounds from swine wastewater treatment system*, in *Journal of Hazardous Materials 152*, 2008, pp. 580-588.

[58] L. Van Zwieten, S. Kimber, S. Morris, K. Chan, A. Downie, J. Rust, S. Joseph, and A. Cowie, *Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility*, in *Plant and soil*, 2010, pp. 235-246.

[59] K. Chan, L. Van Zwieten, I. Meszaros, A. Downie, and S. Joseph, *Agronomic values of greenwaste biochar as a soil amendment*, in *Soil Research*, 2008, pp. 629-634.

[60] J.M. Novak, W.J. Busscher, D.L. Laird, M. Ahmedna, D.W. Watts, and M.A. Niandou, *Impact of biochar amendment on fertility of a southeastern coastal plain soil*, in *Soil Science*, 2009, pp. 105-112.

[61] C.M. McGinley, McGinley, Michael A., *An Odor Index Scale for Policy and Decision Making: Using Ambient and Source Odor Concentrations*, 2006, pp. 8.

[62] T. Florin, *Hydrogen sulphide and total acid-volatile sulphide in faeces, determined with a direct spectrophotometric method*, in *Clinica chimica acta*, 1991, pp. 127-134.

[63] E.A. Magee, C.J. Richardson, R. Hughes, and J.H. Cummings, *Contribution of dietary protein to sulfide production in the large intestine: an in vitro and a controlled feeding study in humans*, in *The American journal of clinical nutrition*, 2000, pp. 1488-1494.

[64] R.M. Stuetz, R.A. Fenner, and G. Engin, *Assessment of odours from sewage treatment works by an electronic nose, H2S analysis and olfactometry*, in *Water Research*, 1999, pp. 453-461.

[65] A. Turk, E. Sakalis, J. Lessuck, H. Karamitsos, and O. Rago, *Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan*, in *Environmental Science & Technology*, American Chemical Society, 1989, pp. 1242-1245.

[66] A. Bagreev, and T.J. Bandosz, *H2S adsorption/oxidation on unmodified activated carbons: importance of prehumidification*, in *Carbon*, 2001, pp. 2303-2311.

[67] T.J. Bandosz, A. Bagreev, F. Adib, and A. Turk, *Unmodified versus Caustics-Impregnated Carbons for Control of Hydrogen Sulfide Emissions from Sewage Treatment Plants*, in *Environmental Science & Technology*, American Chemical Society, 2000, pp. 1069-1074.

[68] F. Adib, A. Bagreev, and T.J. Bandosz, *Analysis of the Relationship between H2S Removal Capacity and Surface Properties of Unimpregnated Activated Carbons*, in *Environmental Science & Technology*, American Chemical Society, 2000, pp. 686-692.

[69] A. Bagreev, and T.J. Bandosz, *On the Mechanism of Hydrogen Sulfide Removal from Moist Air on Catalytic Carbonaceous Adsorbents*, in *Industrial & Engineering Chemistry Research*, American Chemical Society, 2005, pp. 530-538.

[70] F.J. Gutiérrez Ortiz, P.G. Aguilera, and P. Ollero, *Biogas desulfurization by adsorption on thermally treated sewage-sludge*, in *Separation and Purification Technology*, 2014, pp. 200-213.

[71] A. Kaliva, and J. Smith, *Oxidation of low concentrations of hydrogen sulfide by air on a fixed activated carbon bed*, in *The Canadian journal of chemical engineering*, 1983, pp. 208-212.

[72] A.C. Lua, and J. Guo, *Preparation and characterization of chars from oil palm waste*, in *Carbon*, 1998, pp. 1663-1670.

[73] N. Mohamad Nor, L.C. Lau, K.T. Lee, and A.R. Mohamed, *Synthesis of activated carbon from lignocellulosic biomass and its applications in air pollution control—a review*, in *Journal of Environmental Chemical Engineering*, 2013, pp. 658-666.

[74] A. Primavera, A. Trovarelli, P. Andreussi, and G. Dolcetti, *The effect of water in the low-temperature catalytic oxidation of hydrogen sulfide to sulfur over activated carbon*, in *Applied Catalysis A: General*, 1998, pp. 185-192.

[75] M. Steijns, F. Derks, A. Verloop, and P. Mars, *The mechanism of the catalytic oxidation of hydrogen sulfide: II. Kinetics and mechanism of hydrogen sulfide oxidation catalyzed by sulfur*, in *Journal of catalysis*, 1976, pp. 87-95.

[76] Y. Xiao, S. Wang, D. Wu, and Q. Yuan, *Catalytic oxidation of hydrogen sulfide over unmodified and impregnated activated carbon*, in *Separation and Purification Technology*, 2008, pp. 326-332.

[77] Q. Chen, Z. Wang, D. Long, X. Liu, L. Zhan, X. Liang, W. Qiao, and L. Ling, *Role of pore structure of activated carbon fibers in the catalytic oxidation of H2S*, in *Industrial & Engineering Chemistry Research*, 2010, pp. 3152-3159.

[78] M. Steijns, and P. Mars, *Catalytic Oxidation of Hydrogen Sulfide. Influence of Pore Structure and Chemical Composition of Various Porous Substances*, in *Product R&D*, American Chemical Society, 1977, pp. 35-41.

[79] M. Seredych, C. Strydom, and T.J. Bandosz, *Effect of fly ash addition on the removal of hydrogen sulfide from biogas and air on sewage sludge-based composite adsorbents*, in *Waste Management*, 2008, pp. 1983-1992.

[80] Y. Yuan, T. Yuan, D. Wang, J. Tang, and S. Zhou, *Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in an microbial fuel cell*, in *Bioresource Technology*, 2013, pp. 115-120.

[81] E. Setiawati, S. Notodarmojo, P. Soewondo, A.J. Effendi, and B.W. Otok, *Infrastructure Development Strategy for Sustainable Wastewater System by using SEM Method (Case Study Setiabudi and Tebet Districts, South Jakarta)*, in *Procedia Environmental Sciences*, 2013, pp. 685-692.

[82] V. Meeyoo, D.L. Trimm, and N.W. Cant, *Adsorption-Reaction Processes for the Removal of Hydrogen Sulphide from Gas Streams*, in *Journal of Chemical Technology and Biotechnology*, 1997, pp. 411-416.

[83] T. Ganga Devi, and M.P. Kannan, *Calcium catalysis in air gasification of cellulosic chars*, in *Fuel*, 1998, pp. 1825-1830.

[84] A. Bagreev, S. Bashkova, D.C. Locke, and T.J. Bandosz, *Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide*, in *Environmental science & technology*, 2001, pp. 1537-1543.

[85] A. Bagreev, T.J. Bandosz, and D.C. Locke, *Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer*, in *Carbon*, 2001, pp. 1971-1979.

[86] A. Bagreev, and T.J. Bandosz, *H< sub> 2</sub> S Adsorption/Oxidation on Materials Obtained Using Sulfuric Acid Activation of Sewage Sludge-Derived Fertilizer*, in *Journal of colloid and interface science*, 2002, pp. 188-194.

[87] A. Demirbas, *Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues*, in *Journal of Analytical and Applied Pyrolysis*, 2004, pp. 243-248.

[88] M.M.a.A. Quality, *Biofilter design information*, University of Minnesota, 2014.

[89] R. Nicolai, and K. Janni, *Effect of biofilter retention time on emissions from dairy, swine, and poultry buildings*, in *ASAE Annual Meeting*, 1999.

[90] E. Vance, P. Brookes, and D. Jenkinson, *An extraction method for measuring soil microbial biomass C*, in *Soil biology and Biochemistry*, 1987, pp. 703-707.

[91] L. Cihacek, and J. Bremner, *Characterization of the sulfur retained by soils exposed to hydrogen sulfide*, in *Communications in Soil Science & Plant Analysis*, 1993, pp. 85-92.

[92] B. Jorgensen, and J. Postgate, *Ecology of the bacteria of the sulphur cycle with special reference to anoxic-oxic interface environments [and discussion]*, in *Philosophical Transactions of the Royal Society of London. B, Biological Sciences*, 1982, pp. 543-561.

[93] A.G. Boon, *Septicity in sewers: causes, consequences and containment*, in *Water Science and Technology*, 1995, pp. 237-253.

[94] R.L. STARKEY, *ISOLATION OF SOME BACTERIA WHICH OXIDIZE THIOSULFATE*, in *Soil Science*, 1935, pp. 197-220.

[95] C. Black, *Methods of Soil Analysis: Part I Physical and mineralogical properties*, American Society of Agronomy, Madison, Wisconsin, 1965.

[96] P.M. Kopittke, and N.W. Menzies, *A review of the use of the basic cation saturation ratio and the "ideal" soil*, in *Soil Science Society of America Journal*, 2007, pp. 259-265.

[97] G. BÁRCENAS-MORENO, M. GÓMEZ-BRANDÓN, J. Rousk, and E. Bååth, *Adaptation of soil microbial communities to temperature: comparison of fungi and bacteria in a laboratory experiment*, in *Global Change Biology*, 2009, pp. 2950-2957.

Appendices

Appendix I: Odor and Hydrogen Sulfide Quantification Data

Figure 18- Pyrolysis run at 300 °C with a 1 °C ramp rate

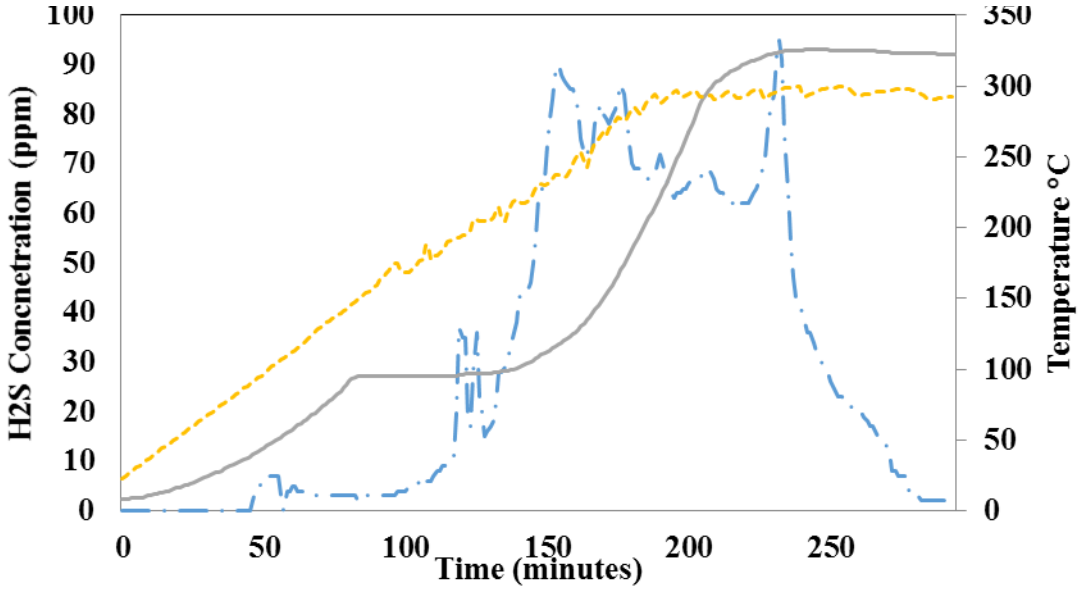


Figure 19- Pyrolysis run at 300 °C with a 3 °C ramp rate

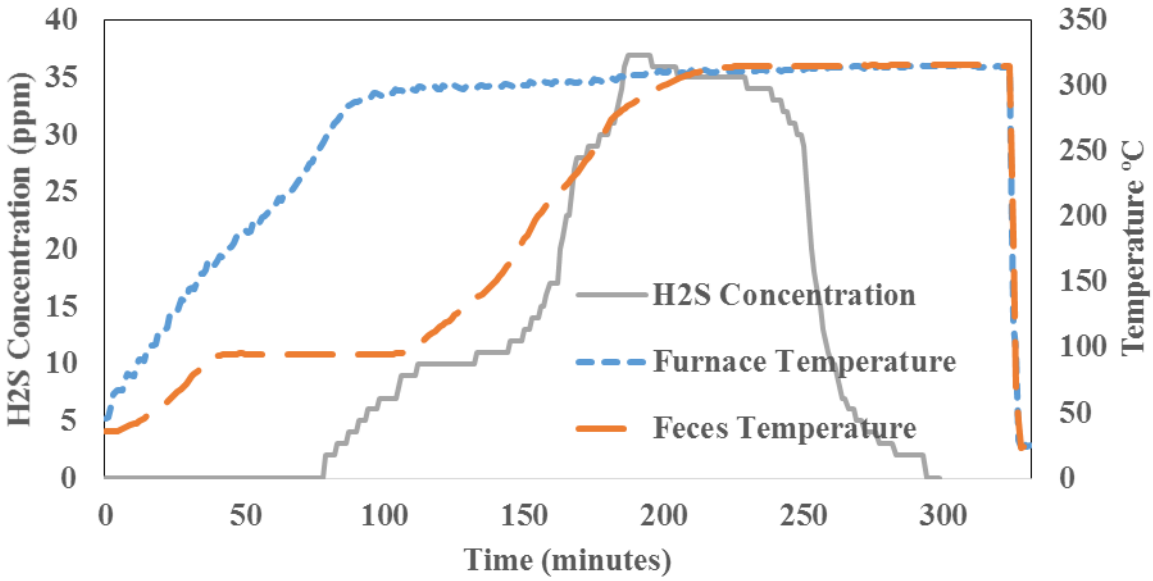


Figure 21- Pyrolysis run at 450 °C with a 5 °C ramp rate

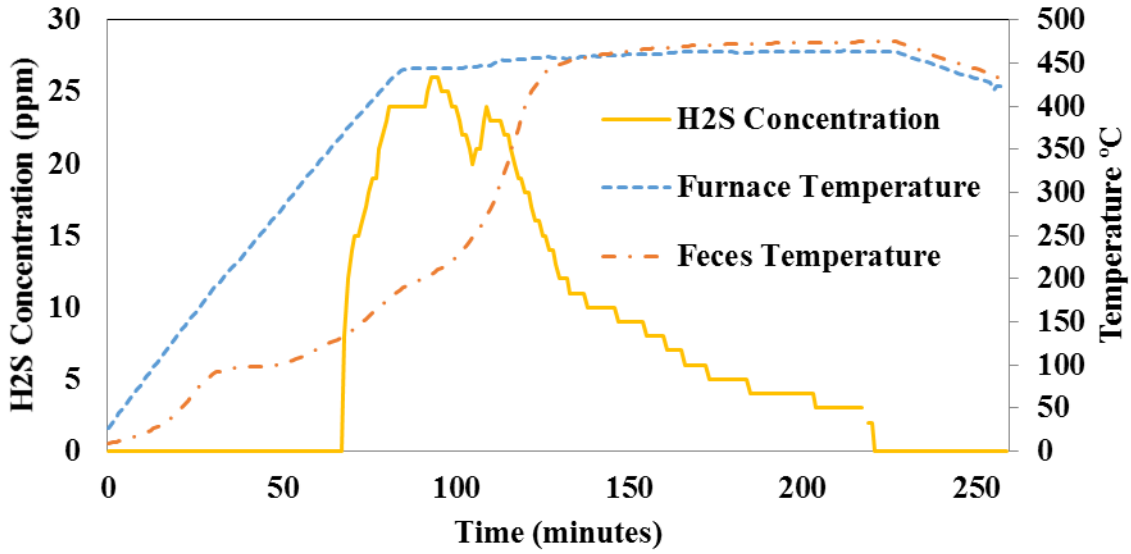


Figure 20- Pyrolysis run at 600 °C with a 5 °C ramp rate

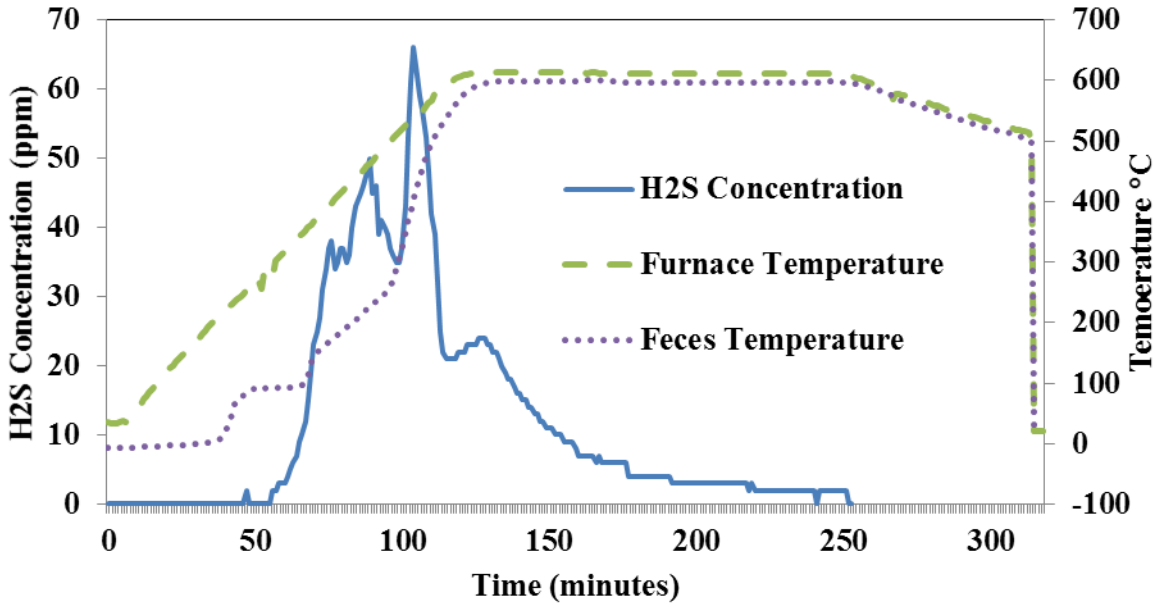
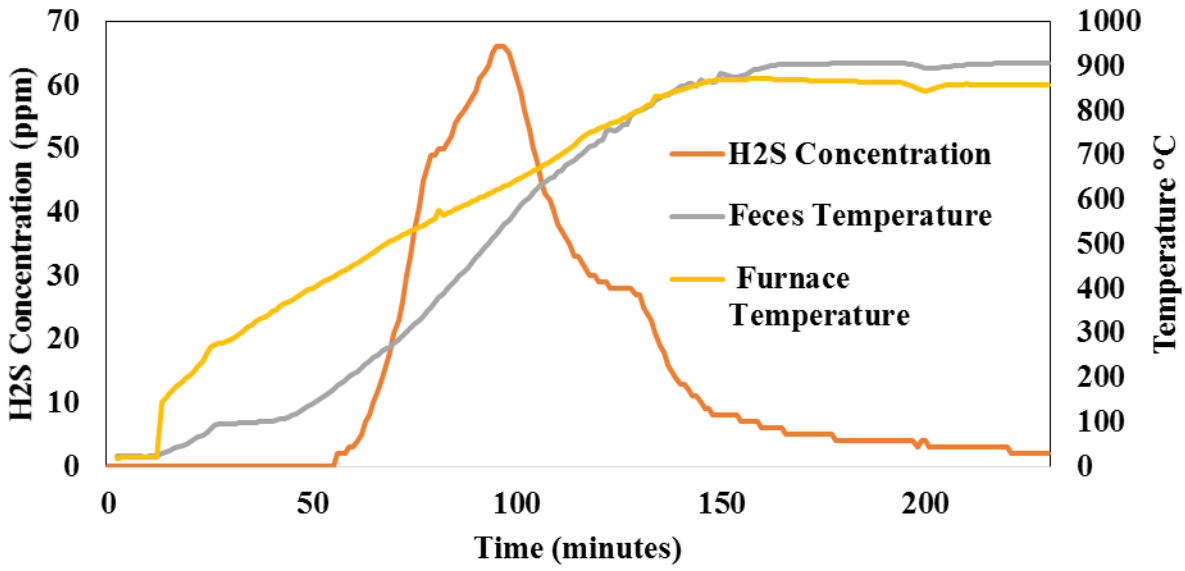


Figure 22- Pyrolysis run at 900 °C with a 5 °C ramp rate



Appendix II: Calculation Tables

Table 19- BET Analysis Data

Relative Pressure	Uptake cc/g (at STP)	Uptake cc/g (at STP)	Uptake cc/g (at STP)	Uptake cc/g (at STP)	Uptake cc/g (at STP)	Uptake cc/g (at STP)	
0.0499	0.137	45.530	33.812	0.375	2.516	21.870	0.075
0.0988	0.163	47.195	35.223	0.702	3.010	23.759	0.100
0.1478	0.180	49.568	35.995	1.018	3.453	25.287	0.115
0.1967	0.192	49.635	36.689	1.337	3.885	26.691	0.128
0.2456	0.203	49.784	37.304	1.654	4.306	28.065	0.139
0.2946	0.214	50.051	37.812	1.970	4.730	29.489	0.151
0.3435	0.224	55.095	38.274	2.287	5.164	30.870	0.160
0.3925	0.232	55.197	38.697	2.601	5.593	32.239	0.171
0.4414	0.242	55.596	39.092	2.918	6.018	33.568	0.181
0.4904	0.252	55.878	39.515	3.234	6.457	34.853	0.191
0.5507	0.265	56.153	39.978	3.553	6.918	36.080	0.203
0.5883	0.278	56.323	40.480	3.875	7.398	37.280	0.218
0.6372	0.291	56.626	40.948	4.197	7.902	38.491	0.232
0.6861	0.311	57.074	41.467	4.522	8.444	39.745	0.250
0.7352	0.333	57.598	41.986	4.854	9.045	41.042	0.272
0.7841	0.360	57.916	42.483	5.191	9.753	42.393	0.301
0.8331	0.395	57.451	42.990	5.540	10.650	43.830	0.344
0.8821	0.448	57.760	43.662	5.918	11.895	45.475	0.416
0.9309	0.543	58.182	44.310	6.383	13.872	47.683	0.587
0.9799	0.878	58.673	45.777	7.563	19.729	52.571	1.867

Breakthrough Capacity

Table 20- Breakthrough capacity for pine and bamboo chars

	300 Pine ADS CAP			**900 Bamboo ADS CAP**			**1200 EC ADS CAP**	
H_2S	87	Vol %	**H_2S**	87	Vol %	**H_2S**	87	Vol %
H_2S	8.70E-05	ml/ml	**H_2S**	0.00008 7	ml/ml	**H_2S**	0.00008 7	ml/ml
F	200	sccm	**F**	200	sccm	**F**	200	sccm
F	80.2628	ml/min	**F**	80.2628	ml/min	**F**	80.2628	ml/min
TBT	1	min	**TBT**	273	min	**TBT**	331	min
Tot Vol	80.2628 7	ml	**Tot Vol**	21911.7 6	ml	**Tot Vol**	26567.0 1	ml
Vol H_2S	6.98E-03	ml	**Vol H_2S**	1.90632 4	ml	**Vol H_2S**	2.31133	ml
n	7.77E-07	mol	**n**	0.00021 2	mol	**n**	0.00025 7	mol
cm^3 char	12.348	cm^3	**cm^3 char**	12.348	cm^3	**cm^3 char**	12.348	cm^3
g char	2.24	g	**g char**	8.69	g	**g char**	1.54	g
g H_2S	0.02642 7	mg	**g H_2S**	7.21463 4	mg	**g H_2S**	8.74741 4	mg
mg/g	0.01179 8	mg/g	**mg/g**	0.83022 3	mg/g	**mg/g**	1.66617 4	mg/g
mg/cm^3	0.00214		**mg/cm^3**	0.58427 6		**mg/cm^3**	0.70840 7	

Table 21- Breakthrough capacity calculations for feces-derived chars

	300 poop ADS CAP			**450 poop ADS CAP**			**900 poop ADS CAP**	
		Vol			Vol			Vol
H_2S	87	%	**H_2S**	87	%	**H_2S**	87	%
	0.00008			0.00008			0.00008	
H_2S	7	ml/ml	**H_2S**	7	ml/ml	**H_2S**	7	ml/ml
F	200	sccm	**F**	200	sccm	**F**	200	sccm
	80.2628	ml/mi		80.2628	ml/mi		80.2628	ml/mi
F	7	n	**F**	7	n	**F**	7	n
TBT	1	min	**TBT**	694	min	**TBT**	7461	min
	80.2628		**Tot**	55702.4			598841.	
Tot Vol	7	ml	**Vol**	3	ml	**Tot Vol**	3	ml
Vol	0.00698		**Vol**	4.84611		**Vol**	52.0991	
H_2S	3	ml	**H_2S**	2	ml	**H_2S**	9	ml
				0.00053			0.00579	
n	7.77E-07	mol	n	9	mol	**n**	9	mol
cm^3			cm^3			**cm^3**		
char	12.348		char	12.348		**char**	12.348	
g char	5.922		g char	5.25		**g char**	6.11	
	0.02642						197.173	
g H_2S	7	mg	g H_2S	18.3405	mg	**g H_2S**	6	mg
	0.00446			3.49342			32.2706	
mg/g	3	mg/g	mg/g	8	mg/g	**mg/g**	3	mg/g
			mg/cm	1.48530			15.9680	
mg/cm^3	0.00214		^{3}	1		**mg/cm^3**	6	

Appendix III: Standard Operating Procedures

Elemental Analysis

1) Samples were weighed in to polypropylene 50 mL tubes and the mass was recorded to the nearest 0.001 g
2) 3 mL of conc. Optima pure nitric acid was added to each sample. Samples pre-digested overnight, cap having a 1/8 inch hole
3) Samples (with caps) were heated in a CEM Mars 5 (open vessel digest) - as follows: 30% (1200 W) power; 15 min step to 95C; hold at 95C for 30 min
4) Samples were cooled.
5) 1 mL of 30% hydrogen peroxide was added to each sample - after effervescence with continued swirling, samples were heated as described above.
6) Samples were cooled.
7) 1 mL of Optima pure hydrochloric acid was added to each sample and heated as described above.
8) Samples were cooled - with the addition of ~10 mL of DI water.
9) Samples were filtered through a #40 Whatman paper filter. The filter was rinsed with DI so as not to exceed a 25 mL volume for the sample
10) Samples were diluted as needed and analyzed on a Perkin Elmer ICP-optical emission spectrometer 8000 against appropriate multi calibration curves.
11) A method blank was carried throughout the procedure and analyzed the same as samples. Sample conc. were blank corrected if needed.

Chloroform Fumigation Direct Extraction Protocol

1) Collect 3 (oven dried) subsamples of 10 g: one for determining gravimetric soil moisture; one non-fumigated sample for immediate extraction; one fumigated sample
2) The Sample to be fumigated should be placed in a 50 mL glass beaker, and put in a vacuum desiccator next to scintillation vial containing boiling chips and 20 mL of ethanol free chloroform. The desiccator can then be evacuated until the chloroform has boiled and then vented. This should be repeated 5 times, without venting the last time. Afterwards, the desiccator should be placed in complete darkness for 3 days. After three days, the extra chloroform can be released by evacuating and venting 10 times.
3) Both the non-fumigated sample and the fumigated sample are then extracted using 50 ml K_2SO_4, placed on the shaker for 1 hour, and then filtered with Whatman No. 1 filter paper.
4) TOC is determined using a TOC analyzer for both fumigated and non-fumigated samples.
5) The difference between carbon in the fumigated and non-fumigated samples is the chloroform-labile C pool (EC) and is proportional to the microbial biomass carbon and indicated in **Equation 4**. The proportionality constant, kEC, is soil specific, but can be estimated at .45 based on previous studies. The above protocol was taken from Vance et al. (1987) [90].

Equation 7- Microbial biomass carbon

$$C = EC/kEC$$

Sulfur Oxidizing Bacteria

1) Create the *Thiobacillus* broth using the recipe in **Table 17**. This recipe is a modification of the original *Thiobacillus* recipe created by Starkey (1935) by HIMEDIA labs [94].

2) After suspending the appropriated amount of each ingredient in distilled water, ensure the medium is completely dissolved. The pH can then be adjusted as desired using sodium hydroxide and hydrochloric acid.
3) Sterilize the broth by autoclaving it at 15 lbs. pressure (121°C) for 15 minutes.
4) Isolate bacteria from soil samples by first diluting 10 grams of soil in 1L of distilled water. Then add 1 mL of that solution to each of the 1 liter broth mixtures
5) Samples are then inoculated into *Thiobacillus* Broth and incubated at 25-30°C for about 7 days or more. Turbidity indicates the growth of *Thiobacillus.*
6) Plates are created using the same recipe as was used to create the broth, but with the addition of agar. The pH can be adjusted in the same way as above.
7) Sterilize the broth by autoclaving it at 15 lbs. pressure (121°C) for 15 minutes.
8) The medium can be poured onto sterile petri plates immediately after it has been autoclaved and incubated at 2-8 °C
9) One mL of broth that has been incubated with samples can be smeared across the top of plates before they are incubated at 30 °C for 7 days before an MPN is obtained

Table 22 - *Thiobacillus* broth and agar ingredients

Ingredients	**Grams / Liter**
Ammonium sulphate	0.400
Monopotassium phosphate	4.000
Calcium chloride	0.250
Ferrous sulphate	0.010
Magnesium sulphate	0.500
Sodium thiosulphate	5.000
*Agar	12.500

.

Porosity

1) A graduated cylinder with 1 L of water should be poured into a 2 L container and a line should be drawn at the point where the water reaches.
2) The water should be disposed of and the 2 L container should be filled with soil up to the marked water line.
3) The graduated cylinder should then be refilled with 1000 mL of water and the water should slowly be poured into the 2 liter container with soil until the water reaches the top of the soil sample.
4) The volume of water remaining in the graduated cylinder should be subtracted from the 1000 mL to calculate the volume of water added to the sample.
5) This volume is equivalent to the pore space in the soil sample. To calculate the % pore space use **Equation 5**.

Equation 8 – Equation for calculating porosity

$$\%\ pore\ space = \frac{pore\ space}{total\ volume} * 100$$

Moisture Content using the Gravimetric Method

1) A soil sample of 10 g should be measured on an aluminum weigh boat. The weight of the aluminum tin and the wet soil and the aluminum tin both need to be recorded.
2) The sample can then be placed in a muffle furnace at 105°C and allowed to dry overnight. Afterward the sample should be weighed and the weight recorded.
3) The process of drying for a few hours and then recording the sample weight should be repeated until there isn't any difference between consecutive measurements.

4) The calculation for moisture content on a dry weight basis can calculated with the formula below in **Equation 6** [95].

Equation 9-Calculation for moisture content on a dry weight basis

$$\theta_d = \frac{(wt\ of\ wet\ soil + tare) - (wt\ of\ dry\ soil + tare)}{(wt\ of\ dry\ soil + tare) - (tare)}$$

pH

1) Soil should be filtered using a sieve so that only the material less than .25 inches is used.
2) Approximately 30 g of soil should be weighed and placed in a glass beaker with 30 g of distilled water.
3) The mixture should be stirred to create a slurry. The slurry then needs to stabilize for a minimum of an hour. During this time the slurry should be stirred every 10 minutes and otherwise it should remain covered.
4) Use an appropriate laboratory pH probe that has been standardized to take pH measurements. The solution should be stirred immediately before the electrodes are immersed. The electrodes should only be immersed into the soil slurry solution, not directly into the soil. Gently turn the beaker to ensure sufficient contact with the electrodes and make sure the pH has stabilized before recording a measurement.