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# Biofiltration Application at Ethanol Plants: Analysis of Aqueous Streams and Treatment of VOCs

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# BIOFILTRATION APPLICATION AT ETHANOL PLANTS: ANALYSIS OF AQUEOUS STREAMS AND TREATMENT OF VOCS

By

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# BIOFILTRATION APPLICATION AT ETHANOL PLANTS: ANALYSIS OF AQUEOUS STREAMS AND TREATMENT OF VOCS

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The United States used 14.5 billion gallons of the biofuel ethanol in 2019 produced primarily (82%) in dry-mill corn ethanol plants. These plants produce volatile organic compounds (VOCs) — some of which are hazardous air pollutants (HAPs) — during production. Traditional treatment methods for gaseous emissions use a large quantity of water or natural gas. Thus, a bio-trickling filter (BTF) is considered an innovative alternative treatment method. A lab-scale BTF was used in this study to look at the effect of ethanol concentration and temperature on the treatment of a HAPs mixture. Gaseous and aqueous testing were performed on the influent and effluent from the BTF. These tests were also completed on select aqueous streams from within two Nebraska ethanol plants (Plants A and B). This thesis concluded that a mesophilic (21ºC) BTF column had a higher removal efficiency for the mixtures tested than a thermophilic (60ºC) column due to pH and VOC solubility. As the concentration of ethanol increased the treatment of acetaldehyde decreased and ethanol removal increased by around 25-35%. This increase may be due to the microbial culture increasing its affinity to ethanol and/or an increase in internal mass transfer of ethanol. It was also found that the microbes had an affinity for VOCs in this order: formaldehyde, ethanol, acetaldehyde, and then methanol. From the aqueous sampling at the two ethanol plants, it was determined that neither of the plants had a stream that met the exact target C:N:P ratio of 200:4:1 that is

necessary for use as a nutrient solution in a BTF. Many of the streams also contained chlorine or excess levels of ethanol— both of which are toxic to microbes. Therefore, the nutrient solution used will be either wastewater treatment plant (WWTP) effluent, a waste stream with nutrients added, or well water with nutrients added. Finally, this thesis concluded that in order for Plant B to meet the impurity limits as set by the federal drug administration (FDA) for ethanol plants transitioning into the production of alcohol-based disinfectants, the column tops or the final product process streams will need to be treated further.

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# CHAPER 1: INTRODUCTION

## 1.1 Introduction

Ethanol is the most cost-effective biofuel available and it can be produced almost anywhere on earth from the fermentation of organic material (primarily corn). Burning this renewable energy resource in vehicles lowers their greenhouse gas emissions (Levac, 2019; Rinkesh, 2021). Ethanol is produced from the fermentation of organic matter, primarily corn. Furthermore, 82% of ethanol is produced in corn dry-mill ethanol plants with 23 of these plants being located in the state of Nebraska (Eidman, 2007; Nebraska Ethanol Board, 2021).

However, during the creation of ethanol through the fermentation of corn at dry-mill ethanol plants, volatile organic compounds (VOCs), some of which are defined as hazardous air pollutants (HAPs) by the US Environmental Protection Agency (EPA), are also created (US EPA, 2015). Traditional methods of treatment for these VOCs at ethanol plants either use a large quantity of water or natural gas. The goal of this research is to reduce the energy, chemical, and water usage associated with traditional treatment methods. The alternative method being looked at here is a bio-trickling filter (BTF), which uses less water than traditional methods, no natural gas, and no chemicals.

This thesis also examines the aqueous and gas-testing results of select aqueous streams from two different Nebraska ethanol plants. The results from these tests further the understanding of their nutrient and compound make-up, and the knowledge gained can give insights into how these streams can be reused or further treated to meet final product needs.

## 1.2 Overview of Ethanol Manufacturing from Corn

As of May 2021, there were 202 ethanol plants in the United States that had a total capacity to produce 17,468 MMgal/yr. of ethanol (BBI International, 2021). Due to the 1973 oil embargo by Arab members of the Organization of Petroleum Exporting Countries (OPEC), an increase in the percentage of ethanol found in gasoline rose throughout the late 1970s and early 1980s to compensate for the reduced oil supply (Office of the Historian, 2016). This caused policies and programs run by both state and the federal government to create incentives for using ethanol in gasoline (US Energy Information Administration, 2020). Though a major tax credit was removed in 2011, consumption of ethanol in the US has gone from about 2 million gallons in 1981 to about 14.5 billion gallons in 2019. This is related in part to ethanol replacing methyl tertiary butyl ether (MTBE) in gasoline, as well as the renewable fuel standard (RFS) requirements under the Energy Independence and Security Act of 2007 (EISA) (US Energy Information Administration, 2020). The RFS requires that 36 billion gallons of renewable fuel be blended into transportation fuel by 2022 (US EPA, 2017).

Ethanol is considered to be one of these renewable fuels. It is called a biofuel in the United States (US) and is produced primarily (97%) from the fermentation of corn. Furthermore 82% of ethanol is produced in dry-mill ethanol plants (Eidman, 2007). There are two different types of corn ethanol plants: dry-mill and wet-mill. The process of wet-milling starts with soaking the corn kernels for up to 48 hours to soften and then further processing the separated corn component into multiple products. This process is usually focused on producing human consumption products rather than ethanol as the main focus. Dry-mill plants, however, grind and then ferment the whole corn kernel, focusing

primarily on peak ethanol production (Smith, 2017). Of the 25 ethanol plants in the state of Nebraska, 23 of them are dry-mill plants (Nebraska Ethanol Board, 2021).

### 1.2.1 Dry-Mill Plant Operation

A general understanding of how a dry-mill ethanol plant operates and what a generic outline of such a plant looks like are explained here as background to this thesis. The processes are outlined in Figure 1.1, which shows an ethanol plant flow diagram.

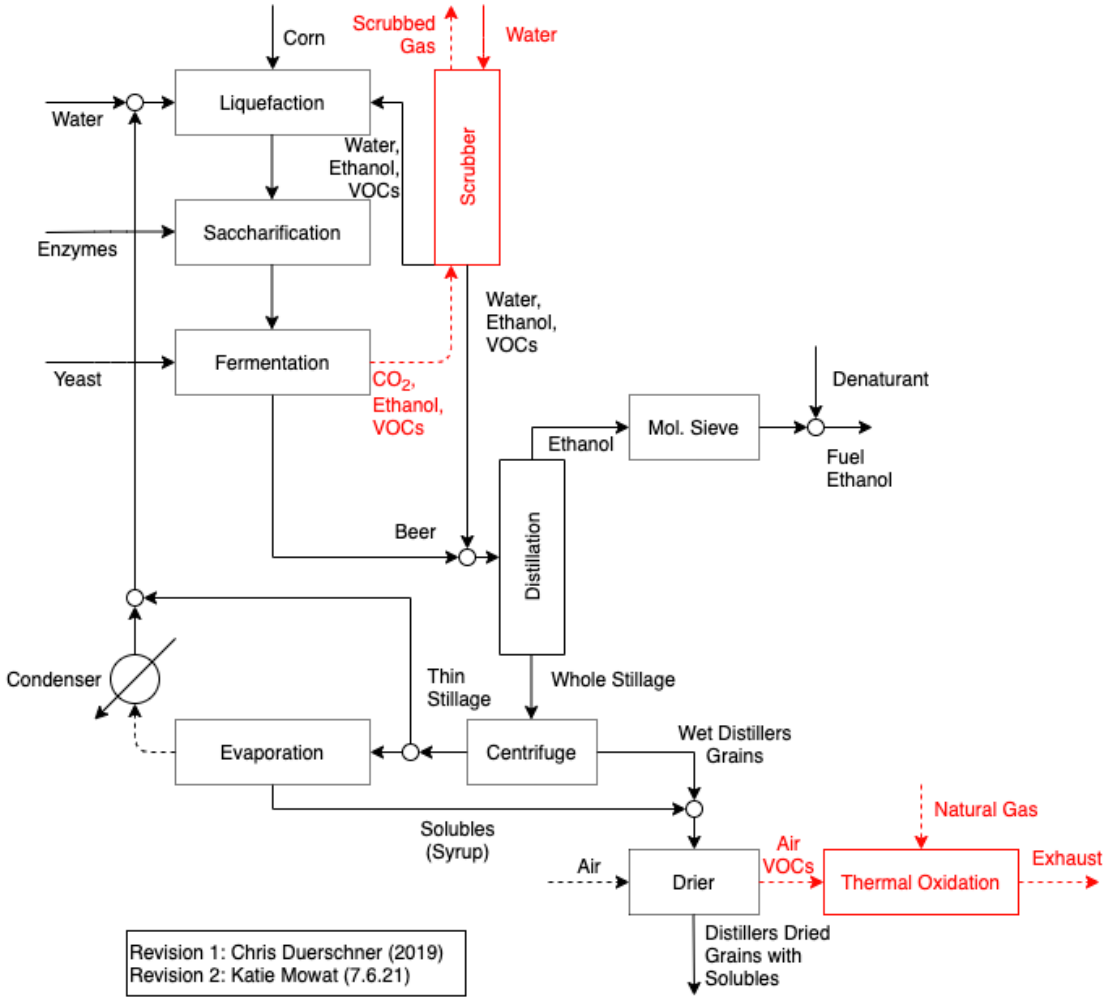



*Figure 1.1-Ethanol Plant Flow Diagram (Solid Lines: Liquid, Dashed Lines: Gas)*

In a dry-mill ethanol plant, the process starts with dry corn being delivered via truck or railcar. The kernels are ground up and before undergoing liquefaction and

saccharification due to the addition of water and enzymes. Next, yeast is added to the mixture and fermentation starts. During fermentation equimolar amounts of carbon dioxide ($CO_2$) and ethanol are produced. VOCs are also released in this exhaust stream. The exhaust stream from the fermenter is then directed to a $CO_2$ scrubber for treatment (shown in red in Figure 1.1).

Next, the fermented corn moves into the beer well where ethanol formation continues until it passes into the distillation column. From the distillation column 190-proof ethyl alcohol distillate is produced from the top and whole stillage from the bottom. The ethyl alcohol distillate is then sent through molecular sieves to produce 200-proof fuel-grade ethanol. The whole stillage or "bottoms" has a moisture content of approximately 87% (Yang & Rosentrater, 2015), and it is split into thin stillage and wet distillers grains using a centrifuge. The thin stillage, which has a moisture content of approximately 92% (Yang & Rosentrater, 2015), is again split with some going back to the beginning of the process while the rest goes through evaporation to produce solubles (Duerschner, 2019).

The wet distillers grains and solubles are then recombined in a drying process, using a rotary drum dryer, that produces distillers dried grains with solubles (DDGS). During the drying process, an exhaust stream containing VOCs is released and sent to a thermal oxidizer for treatment (shown in red in Figure 1.1).

DDGS are sold as a high protein additive for livestock and poultry feed. The selling of this byproduct of ethanol production is a major component to the economic viability of the production. Every bushel of corn that is sent through a dry-mill ethanol plant

produces approximately 2.85 gallons of ethanol fuel and 18.2 pounds of DDGS (Duerschner, 2019; McAlcoon et al., 2000).

## 1.3 Traditional Methods of Air Pollution Control

As mentioned above, during the production of ethanol, VOCs are released. Some of the compounds in these ethanol plant exhaust streams include acetaldehyde, formaldehyde, acrolein, methanol, ethanol, and acetic acid (Brady & Pratt, 2007). Furthermore, some of these VOCs are listed on the US Environmental Protection Agency's (EPA) list of hazardous air pollutants (HAPs) (US EPA, 2015). The EPA regulates the quantity of HAPs each plant is allowed to release into the environment (US EPA, 2021). The total emissions from a plant are limited to 10 tons per year for each individual HAP and 25 tons per year for the total HAPs emissions per plant in order for a plant to maintain an area source status under the US EPA (US EPA, 2019; US EPA Region 7, 2007). These amounts are stipulated by the National Emission Standard for Hazardous Air Pollutants (NESHAP) and Miscellaneous Organic National Emission Standard for Hazardous Air Pollutants (MONs) (US EPA, 2013b).

As mentioned above in Section 1.2.1, there are two places where VOCs are released in the ethanol plant: during fermentation and during the drying of DDGS. There are two traditional air pollution control methods that are currently used in ethanol plants: a carbon dioxide ($CO_2$) scrubber and a regenerative thermal oxidizer (Brady & Pratt, 2007).

### 1.3.1 Carbon Dioxide ($CO_2$) Scrubber

$CO_2$ scrubbers are currently being used to remove the HAPs from the exhaust exiting the fermenters. The process depends on water to dissolve volatile HAPs back into

the liquid stream instead of the gaseous state. The scrubber operates by providing a large contact surface area, a packed bed, between the gas and the water that flow counter to each other. Additionally, sodium bisulfite is added to some scrubbers to increase the aqueous stability of aldehydes (acetaldehyde, formaldehyde and acrolein) by formation of bisulfite adducts. The water is subsequently recycled back into the fermenter in order to capture as much ethanol from the stream as possible. The rest of the gas, which is composed mostly of $CO_2$, is released into the atmosphere (Bryan, 2003). For a 100 MMgal/yr. plant, approximately 385 million gallons of water will be used annually for $CO_2$ scrubbers alone (Duerschner, 2019).

### 1.3.2 Regenerative Thermal Oxidizer (RTO)

Thermal oxidization is another common method that is used to treat HAPs. After ethanol is removed from the fermented solution, part of the remaining material is called thin stillage. In order to improve the shelf life, and for transportation to farms for cattle feed, the thin stillage is further dried. During the drying process, volatile HAPs are released. The exhaust from the dryer is treated via combustion with in a regenerative thermal oxidizer (RTO). The RTO uses natural gas to burn off the HAPs in the exhaust (Bryan, 2003). An ethanol plant producing 55 million gallons of denatured ethanol annually will size its RTO for approximately 18 MMBtu/h and will burn approximately 155 million standard cubic feet (SCF) of natural gas each year (Duerschner, 2019).

## 1.4 Bio-Trickling Filter (BTF)

The idea of using a biological filter for treatment of odorous gases from wastewater treatment plants (WWTPs) was first proposed in 1923. The first bioscrubbers were installed in the 1970s with the first BTF coming into use around 1973 (van Groenestijn,

2005). Over the last 30 years the applications of bioscrubbers and BTFs have increased significantly. BTFs are now widely employed at WWTPs for odor control (Prado et al., 2008). They are also seen as an innovative alternative to traditional physical-chemical gas treatment technologies and, in the case of this study, BTFs are being assessed as a replacement for $CO_2$ scrubbers and RTOs in ethanol plants.

Since traditional treatment processes use either a significant amount of water or energy (natural gas) to operate, the utilization of a bio-trickling filter (BTF) is proposed as an innovative industrial HAPs treatment method (Chen et al., 2010). BTFs are made up of a column, a media to support microbial growth, microbial seed, a gas stream that contains oxygen, and a nutrient stream to feed the microbes (Delhoménie & Heitz, 2005). BTFs use less water (about 0.5% of the amount needed for a $CO_2$ scrubber) and energy (no natural gas) than $CO_2$ scrubbers and RTOs.

Due to high wastewater treatment costs, most plants attempt to operate under a "zero-water-waste" model. In order to implement this model, water from condenser processes, a portion of thin stillage, and water from the $CO_2$ scrubber are recycled back to the liquefaction stage to limit the need for supplementary freshwater addition. These recycled waters are processed before reentering the process stream. By lowering the amount of water needed, plants will not need to foot the cost of these recycling procedures (Duerschner, 2019).

BTFs are able to function on about 0.5% of the water that $CO_2$ scrubbers need to operate. The two systems function somewhat similarly, as both have a packed bed of biological support media. However, only a small amount of "trickling" fluid (nutrient solution) is needed to support the biomass in a BTF, and flow is generally co-current.

BTFs also degrade many dilute VOCs instead of recycling them and other impurities back into the fermentation tank. Thus, cost-wise and water-wise BTFs are an appealing alternative to $CO_2$ scrubbers.

There are a few common obstacles that face the use of BTFs however. Some of these include hydrophobic or insoluble VOCs, variable loading rates, and periods of no loading. In the case of VOCs at ethanol plants, the exhaust is usually made up of short-chain aldehydes and alcohols. These are soluble in water and thus will be treated in the BTF. Shutdowns are usually scheduled and only happen a few times a year. Variable loading rates may still be a problem. Table 1.1 summarizes some of the advantages and disadvantages of the BTF in comparison to the other aforementioned common treatment methods.

Other issues that could arise when using a BTF to treat ethanol exhaust fumes are the temperature of DDGS-dryer exhaust and the composition of fermentation-tank exhaust. Gasses leave the dryer at temperatures ranging from 100-140 °C, however, after passing through a cyclone or other particulate matter (PM) control device, the temperature is reduced to at most 60°C. Few studies on the thermophilic treatment of VOCs have been completed, so the effectiveness of a BTF in thermophilic conditions for treating an ethanol exhaust stream is uncertain.

The exhaust from the fermenter has a high concentration of ethanol and lacks oxygen. High concentrations of VOCs in the fermenter exhaust can cause excess biomass growth that limits the ability of the BTF to work effectively (pressure drops and flow-path channeling). A second issue would be the unequal concentrations of VOCs in the exhaust stream. A VOC with a significantly higher concentration may cause

microorganisms responsible for its degradation to outcompete strains able to degrade the more dilute VOC components. It is also not in the ethanol producers' best interest to biodegrade large quantities of ethanol as the ethanol could be recovered and sold for profit.

*Table 1.1-Advantages and Disadvantages of Common Ethanol Plant Treatment Methods and BTFs*

| **Comparison Technology** | **Advantages** | **Disadvantages** |
|---|---|---|
| $CO_2$ Scrubber | • Quick start-up<br>• Simple to operate<br>• Recovers ethanol vapors | • Large amounts of water required<br>• Addition of sodium bisulfate<br>• Only effective for water soluble compounds |
| Regenerative Thermal Oxidizer | • Quick start-up<br>• Efficient at destroying VOCs<br>• Is not selective based on solubility or biodegradability of the compounds it degrades | • Natural gas required for operation<br>• High carbon footprint<br>• High cost of maintenance annually |
| Bio-Trickling Filter | • Less water required<br>• High removal efficiency attainable<br>• Could potentially use a recycled ethanol plant stream for nutrient solution<br>• Less carbon footprint<br>• No natural gas required | • Longer start-up procedure<br>• Variations in loading rates affect performance<br>• Less effective for insoluble compounds<br>• Cannot handle extremely hot air streams<br>• Can biodegrade ethanol (valuable resource) |

There are luckily some options to adapt a BTF to meet these aforementioned challenges. Placing a smaller scrubber without chemical addition upstream of the BTF can help to recover ethanol and reduce its concentration to values similar to the other exhaust components. The smaller scrubber would not require any sodium bisulfite since aldehydes would be removed in the BTF instead of in the scrubber. Another alternative

would be to mix the fermenter and DDGS-dryer air streams together. The DDGS-dryer stream would add oxygen to the fermenter stream and dilute the ethanol vapors by approximately 1:45. The mixture would also help to partially cool the dryer exhaust. Other conventional methods could also be used to further cool the dryer exhaust stream.

## 1.5 Goals and Objectives

The main goal of this thesis is to evaluate the feasibility of using a BTF to treat VOCs from ethanol plant exhaust. In order to evaluate this, the treatment of a synthetic ethanol plant exhaust mixture of acetaldehyde, formaldehyde, methanol, and two different concentrations of ethanol will be assessed in a lab-scale BTF. Past research has proven that singularly acetaldehyde, formaldehyde, and methanol can be effectively biodegraded at levels similar to those found in ethanol plant exhaust and in both mesophilic (21ºC) and thermophilic (60ºC) conditions (Al-Faliti, 2020; Duerschner, 2019). However, a study has yet to be completed on the treatment of a synthetic ethanol plant stream mixture in a BTF under mesophilic and thermophilic conditions.

Additional goals of this thesis are to analyze select liquid streams from ethanol plants. There are two reasons behind this type of analysis. The first is to evaluate ethanol plant streams as potential nutrient solutions for a BTF. The second reason is to look at the levels of impurities in different streams in order to determine where additional treatment is necessary in order to produce a product that meets the US Food and Drug Administration's (FDA) regulations for impurities in hand sanitizer.

Thus, the objectives of this thesis are to:

1. Examine the treatment of a Mixture of HAPs with different ethanol concentrations in a BTF.

2. Evaluate ethanol plant liquid streams to identify if any can be used as a nutrient stream for a BTF.
3. Examine the ethanol plant liquid streams for impurities in order to determine where further treatment is needed in order for the final ethanol product to meet FDA standard impurity levels.

## 1.6 Organization of Thesis

This thesis is made up of six chapters. The first chapter is the introduction. The introduction gives an overview of the ethanol industry in the US and the manufacturing process of ethanol from corn. It further details the traditional methods of air pollution control and how a BTF is an innovative VOC treatment option. Chapter 1 also contains the goals and objectives of this thesis and its organization. Chapter 2 is a review of the related literature. It introduces the physical and chemical properties of acetaldehyde, formaldehyde, acrolein, methanol, and ethanol as well as their impact on human health. Chapter 2 also reviews the literature on biodegradation of mixtures in BTFs and the thermophilic effect on the treatment of mixtures in BTFs. Finally, this section reviews the relevant literature on the make-up of nutrient solutions for BTFs.

Chapter 3 describes the methods and materials used in the studies in this thesis. It reviews both aqueous and gas-sample analyses. The locations and descriptions of ethanol plant streams and sample collection processes are also listed in this chapter. This section concludes with an overview of the operation and design of a BTF.

Chapter 4 is written as a stand-alone manuscript that will be submitted to a journal for publication. It includes the methods and results of the study investigating the

biodegradation of HAPs mixtures with different ethanol concentrations under mesophilic and thermophilic conditions.

Chapter 5 contains the results of liquid-stream analyses for select streams from two different ethanol plants (Plant A and Plant B). These results lead first to conclusions about the potential of these streams to be used as possible nutrient solutions for a BTF. Further results and analysis of the streams from Plant B look at the levels of impurities in different streams. These results help to determine where additional treatment is necessary in order to produce a product that meets the FDA regulations for impurities in hand sanitizer. Portions of the material in Chapter 5 have been published in a manuscript titled "Compliance with Hand Sanitizer Quality During the SARS-CoV-2 Pandemic: Assessing the Impurities in an Ethanol Plant" which was published in the Journal of Environmental Management in late 2021. The author of this thesis was one of the contributing authors to this paper (Cohen et al. 2021). Chapter 6 is composed of thesis conclusions and recommendations for future work.

# CHAPER 2: LITERATURE REVIEW

## 2.1 Introduction

The treatment of mixtures containing volatile organic compounds (VOCs), released during ethanol production, is the basis for the research in this thesis. This chapter considers in further detail the use of lab-scale bio-trickling filters (BTFs) for treating (VOCs). This thesis particularly evaluates VOC compounds that have been categorized by the Environmental Protection Agency (EPA) as hazardous air pollutants (HAPs) (US EPA, 2015). This chapter will give details on the physical and chemical properties, as well as the human-health impacts of these HAP compounds common to ethanol plant exhaust: acetaldehyde, formaldehyde, acrolein, and methanol. Ethanol is another VOC that is common to ethanol plant exhaust and will be described, however it is not recognized as a HAP.

As mentioned in Section 1.4, BTFs have evolved from being used only as odor-emissions control methods to being considered alternatives to traditional physical-chemical gas treatment technologies in the last 30 years. BTFs can be used to treat waste gases from a variety of chemical processes while using less energy and water than traditional methods and producing less carbon emissions. This project explores the use of BTFs as a possible replacement for current ethanol plant exhaust treatment methods for these reasons.

Past research and literature reviews by Duerschner (2019), Al-Faliti (2020), and Balasubramanian et al. (2012) have shown that there have been numerous biofiltration studies that focused on the treatment of single VOCs. Some of the compounds studied

include hydrocarbons (e.g., benzene, styrene, hexane, toluene, and naphthalene), oxygenated hydrocarbons (e.g., methanol, ethanol,), ketones (e.g., acetone and methyl ethyl ketone), chlorinated hydrocarbons (e.g., chlorobenzene and o-dichlorobenzene), and sulfur compounds (e.g., hydrogen sulfide) (Balasubramanian et al., 2012). The results from Duerschner (2019) and Al-Faliti (2020)'s studies showed that acetaldehyde, formaldehyde, and methanol — all common HAPs in ethanol plant exhaust — can be treated individually in a BTF. Thus, this chapter will look at the simultaneous treatment of multiple compounds or mixtures and how they degrade in BTFs. The interaction between the BTF columns and the mixtures will further the understanding of the results in the study explained in Chapter 4. Since the exhaust flow temperature may vary at different stages of the treatment process, studies on the thermophilic effect on mixtures will also be discussed.

BTFs depend on a nutrient solution that is tricked through the BTF column at a regular interval to keep the microorganisms healthy and fed. This chapter will include a summary of the nutrient solutions used by different studies.

## 2.2 Characteristics of Compounds Found in the Exhaust of Ethanol Production

The exhaust from an ethanol plant contains multiple HAPs. The following compounds are listed on the EPA's list of HAPs: acetaldehyde, formaldehyde, acrolein, and methanol (US EPA, 2015). Ethanol is not listed as a HAP but is still a common compound found in the ethanol plant exhaust. Acetaldehyde, formaldehyde, and acrolein are aldehydes. Aldehydes are made up of a carbonyl group with a hydrogen atom and either an aliphatic or aromatic organic group attached. These compounds are created

through the oxidation of alcohols (NOAA, n.d.). Ethanol and methanol are both alcohols. A list of physical properties of the aforementioned compounds are presented in Table 2.1

*Table 2.1-Physical and Chemical Properties of VOCs Found in Ethanol Plant Exhaust*

| Property | Acetaldehyde | Formaldehyde | Acrolein | Methanol | Ethanol |
|---|---|---|---|---|---|
| Molar Mass (g/mol) | 44.05[f] | 30.03[f] | 56.07[f] | 32.04[f] | 46.07[f] |
| Density (g/mL) | 0.788[f] | 0.815[f] | 0.841[f] | 0.7913[f] | 0.7894[f] |
| Boiling Point (°C) | 21[f] | -19.5[f] | 49[f] | 64.7[f] | 78.3[f] |
| Vapor Pressure at 20 °C (mmHg) | 750[g] | 52[c] | 210[h] | 97[j] | 44.6[j] |
| Solubility in Water | Miscible[f] | Miscible[f] | Soluble 21 parts in 100[f] | Miscible[f] | Miscible[f] |
| Henry's Law Constant (atm $m^3$/mol) | $8.8x10^{-2}$[e] | $3.4x10^{-4}$[e] | - | - | - |
| Odor Threshold (ppm) | 0.05[i] | 0.5[c] | <0.1[a] | 33[d] | 0.52[b] |

a-(Beauchamp Jr et al., 1985)
b-(ChemicalBook, 2017a)
c-(ChemicalBook, 2017b)
d-(ChemicalBook, 2017c)
e-(Chen, 2009)
f-(Dean, 1992)
g-(Fisher Scientific, 2008)
h-(OSHA, 2018)
i-(US EPA, 2000)
j-(*Vapor Pressure Calculator*, 2019)

### 2.2.1 Acetaldehyde

Acetaldehyde is a two-carbon aldehyde. Its chemical formula is $C_2H_4O$. This compound oxidizes readily to form unstable peroxides. It is flammable, volatile, and could spontaneously explode. Acetaldehyde is listed on the EPA's list of HAPs under CAS number 75070. Acetaldehyde is used as an intermediate in the synthesis of other chemicals and as a preservative (US EPA, 2000). The EPA's Integrated Risk Information System (IRIS) works to identify and characterize the health hazards of chemicals found in the environment (US EPA, 2013a). According to their weight of evidence (WOE) for

cancer characterization, acetaldehyde is listed as B2 (probable human carcinogen-based on sufficient evidence of carcinogenicity in animals) (US EPA, 1988). This is based on evidence of increased nasal tumors in rats and laryngeal tumors in hamsters after inhalation of acetaldehyde.

### 2.2.2 Formaldehyde

Formaldehyde ($CH_2O$) is a one-carbon aldehyde. It is used in making building materials, many household products, personal-care products, and as a preservative in funeral homes and medical labs (American Cancer Society, 2014). Formaldehyde is highly volatile and flammable. In order to perform tests in the lab, a formalin solution containing 37% formaldehyde solution was used. This solution is still flammable, toxic, and hazardous (Fisher Scientific, 2019). Formaldehyde is listed as CAS number 50000 on the EPA's HAPs list. Based on the EPA's IRIS, formaldehyde is given a WOE B1 (probable human carcinogen-based on limited evidence of carcinogenicity in humans) characterization (US EPA, 1991). Nine studies have shown a statistically significant association between inhalation of formaldehyde by humans and cancer. Multiple studies on rats and mice also show an increase in nasal cancer after long-term inhalation. If ingested it can cause sudden death (Fischer, 1905).

### 2.2.3 Acrolein

Acrolein is also an aldehyde, and its chemical formula is $C_3H_4O$. It is flammable, highly toxic if inhaled, ingested, or absorbed, corrosive, and carcinogenic (Sigma-Aldrich, 2012). Acrolein is CAS number 107028 on the EPA's HAPs list. No WOE characterization has been assigned to Acrolein due to a lack of studies on the subject.

However, case studies compiled by Bast et al., (2010) show both its nonlethal toxicity and acute lethality.

### 2.2.4 Methanol

Methanol is an alcohol with a chemical formula of $CH_3OH$. It is also called wood alcohol and methyl alcohol. It is used to create fuel, solvents, and antifreeze (ChemicalSafetyFacts, 2017). Methanol is highly flammable, toxic if inhaled, ingested, or absorbed, and a health hazard (Fisher Scientific, 2015). Methanol's CAS number on the EPA's HAPs list is 67561. Studies have shown negative developmental effects in mice that have been exposed to methanol. However, no WOE characterization has been listed.

### 2.2.5 Ethanol

Ethanol or ethyl alcohol is used to make alcoholic beverages, used in personal care products, used as a disinfectant, and is added to fuel (ChemicalSafetyFacts, 2014). Its chemical formula is $C_2H_5OH$. Ethanol is CAS number 64175 but is not listed on the EPA's HAPs list. The compound is volatile, however, and flammable. It is also toxic if ingested. It can cause drowsiness or dizziness if inhaled, can damage fertility or an unborn child, and can affect organs if there is prolonged or repeated exposure (Fisher Scientific, 2014). Ethanol can cause alcohol poisoning and death at concentrations around 80-90 mmol/L (Perri et al., 2019). A concentration of around 6.25% by volume inhibits the growth of bacteria such as E. coli (Man et al., 2017), and ethanol at lower concentrations than that slows bacterial growth.

### 2.2.6 Biodegradation of Ethanol Plant Exhaust Compounds

Compounds, such as those in ethanol plant exhaust, are broken down during biodegradation. Ethanol is broken down into acetaldehyde—another of the compounds

found in ethanol plant exhaust. Acetaldehyde is further broken down into acetate and acetic acid (NIAAA, 2007; Hipólito et al., 2007)). Microbes break methanol down into formaldehyde, formic acid, and formate (Costa & Aschner, 2014). Formaldehyde—another ethanol plant exhaust compound—is broken down into formic acid and formate (American Cancer Society, 2014). The breakdown of these compounds found in ethanol plant exhaust by microbes—biodegradation—results in different kinds of acids.

## 2.3 Biodegradation of Mixtures in Bio-Trickling Filters (BTFs)

As mentioned in the introduction, BTFs are used to treat HAPs found in ethanol plant exhaust. Some of the common compounds found in an ethanol plant exhaust stream are acetaldehyde, formaldehyde, acrolein, methanol, and ethanol (Schill, 2019). However, treating mixtures can create complex microbial system interactions. Balasubramanian et al. (2012) points this out by looking at two different studies. The addition of ethanol significantly increases the o-dichlorobenzene removal rates in the Bhattacharya & Baltzis (2001) study, but ethanol negatively affects the degradation of toluene and benzene due to causing oxygen limitations in the Lovanh et al. (2002) study. These oxygen limitations are due to the fact that the metabolic flux of the substrate is not proportional to its availability. In Lovanh et al.'s case, the consumption is ethanol-driven, thus the oxygen and nutrients are consumed by the breakdown of ethanol leaving none for the breakdown of toluene and benzene. Table 2.2 compiles a list of studies that look at mixtures of VOCs being treated by BTFs. The terminology used in Table 2.2 is as follows: empty bed residence time (EBRT), loading rate (LR), and elimination capacity (EC). EBRT is the ratio of the total bed volume to the air flow rate. LR is the rate at which a VOC enters the

BTF and the EC is the rate that the VOC is biodegraded. Both have units of grams of VOC per cubic meter of bed volume per hour.

The effect of mixtures on the biodegradation of single VOCs is complex. Recent studies listed in Table 2.2 show that solubility, biodegradation rate, compound loadings, pH, nutrient solution composition, and oxygen limitations can influence the biodegradation of different compounds within the mixture.

In the study completed by Prado et al. (2008), solubility played a part in the biodegradation. Though formaldehyde and methanol had removal efficiencies of around 100% between two their two stage biofilters, dimethyl ether only had a removal efficiency of 12%. They attribute this to the lower solubility of the compound and a slower biodegradation rate. Prado et al. (2008) also determined that this method of treatment was able to treat the mixture of VOCs commonly found in the gaseous emissions from formaldehyde-resin-producing industries at concentrations comparable to those observed in actual industrial emissions.

*Table 2.2-Studies Looking at the Treatment of VOC Mixtures in Bioscrubbers*

| **Authors** | **Compounds** | **EBRT (sec)** | **Media** | **Max EC (g $m^{-3}$ $h^{-1}$) or Removal Efficiency (%)** | **LR @ Max EC (g $m^{-3}$ $h^{-1}$)** | **Inlet Concentration ($ppm_v$)** | **Comments** |
|---|---|---|---|---|---|---|---|
| Prado et al., 2008 | Formaldehyde<br>Methanol<br>Dimethyl ether<br>Carbon Monoxide | 60 | Lava Rock | 100%<br>100%<br>12%<br>80% | | N/A | |
| Chen et al., 2010 | Acetaldehyde<br>Formaldehyde<br>Ethanol<br>Acetic Acid | 10<br>20 | Diatomaceous earth | 62%<br>99%<br>57%<br>98% | 27<br>12<br>61<br>36 | 40<br>27<br>89<br>80 | Results at a pH of 4.6. Acetaldehyde decreased from 95% to 62% as pH decreased from 7 to 4.6 |
| Jamshidi et al., 2017 | Formaldehyde<br>Acetaldehyde<br>Acrolein | 120 | Compost-scoria-sugarcane bagasse (6:2:2 vol ratio) | 0.9<br>1.5<br>0.65 | 15<br>2<br>0.85 | 7.58-9.5<br>7.58-6.5<br>3.2-4 | |
| Prado et al., 2004 | Formaldehyde<br>Methanol | 71.1 | Lava Rock | 41.2<br>2.3 | 46.2<br>4 | N/A | |

*Table 2.3-Studies Looking at the Treatment of VOC Mixtures in Bioscrubbers (Continued)*

| **Authors** | **Compounds** | **EBRT (sec)** | **Media** | **Max EC (g $m^{-3}$ $h^{-1}$) or Removal Efficiency (%)** | **LR @ Max EC (g $m^{-3}$ $h^{-1}$)** | **Inlet Concentration ($ppm_v$)** | **Comments** |
|---|---|---|---|---|---|---|---|
| Aly Hassan & Sorial, 2011 | n-hexane<br>Benzene | 120 | Diatomaceous earth | 10.3<br>36.8 | 21.1<br>42.7 | 199<br>445.1 | |
| Zehraoui et al., 2012 | n-hexane<br>Methanol | 120 | Diatomaceous earth | 8.4<br>63.7 | 13.2<br>64.5 | 127<br>974.9 | |

Loading rate can influence biodegradation of single compounds. Chen et al. (2010) points out that "in [their] study ~15 g/m$^3$ h of formaldehyde was readily degraded in the presence of 0.5–26 g/m$^3$ h methanol at an EBRT of 80 s" but in other studies, such as Prado et al. (2004), the methanol loadings can increase to a point where there is "complete inhibition of formaldehyde removal from [a] system." Chen et al.'s study also looked at the effect of pH on the biodegradation of a mixture of acetaldehyde, ethanol, formaldehyde, and acetic acid. They found that the removal efficiency of acetaldehyde decreased from 95% at a pH of 7 to 62% at a pH of 4.6. The removal efficiencies of the other compounds, especially ethanol, also decreased. The decrease in pH could happen naturally after extended operation and a buildup of acetic acid, but in the case of this study a low pH was achieved quickly by using the nutrient solution to lower the pH.

Jamshidi et al. (2017) points out in their study that there are optimum influent concentrations of pollutants for peak removal efficiency. If the concentration is too high, the BTF will not have enough time to treat it. Higher amounts of aldehydes can also be toxic to the BTF.

Bak et al. (2017) looked at the treatment of a styrene, ethanol, and dimethyl sulfide mixture in a contaminated airstream using a compact trickle-bed bioreactor. However, this study was focused mostly on the bacterial consortium composition. The study did find that ethanol biodegradation was near 100% at all concentrations, but the removal efficiency decreased for the mixture as the contaminant loads increased. The pH was optimized to 7.0 +/- 0.15 (Bak et al., 2017).

A study performed by Prado et al. (2004) determined that methanol is a more accessible carbon source for microorganisms than formaldehyde. This explains the fact

that there is no formaldehyde removal at high methanol loading rates. This study also looked at nutrient solution frequency and pH. They determined that the nutrient solution should be renewed weekly and inadequate liquid or nutrient content will negatively affect removal efficiency. As seen in other studies, they also found that a low pH adversely affects results.

The Zehraoui et al. (2012) study examined the effect of methanol on the removal of hydrophobic n-Hexane. Their results showed that methanol increased the bioavailability of n-hexane even at concentrations that affected n-hexane's biodegradability. This means that, for the compounds being degraded, it is important to consider how soluble they are in water. Solubility is important in order for the compounds to interface with the biofilm in the BTF within the EBRT.

## 2.4 Thermophilic Effect on BTF Treatment of Mixtures

There are two ethanol plant exhaust streams that a BTF could treat: the exhaust from the fermentation tanks or the exhaust from drying the DDGS. The fermentation tank exhaust is at room temperature. Thus, studies mentioned in Section 2.4 are applicable in comparing possible results for treating a VOC mixture such as the fermentation exhaust stream. However, the exhaust from the DDGS is around 100-140°C and after particulates are removed the stream is cooled down to about 60°C (Chen et al., 2010).

Duerschner (2019) and Al-Faliti (2020) have both compiled literature on the treatment of single VOCs in BTFs under thermophilic conditions. However, there have not yet been many comparable studies focused on BTFs treating mixtures under thermophilic conditions. Luvsanjamba et al. (2007) is one of these few studies. This study operated two BTFs in parallel; one at ambient temperature and the other at 52°C

(thermophilic). Higher elimination capacities of isobutyraldehyde and 2-pentanone were reached in the thermophilic BTF. The study also found that the reactor at ambient temperature experienced problems with foam formation, higher biomass accumulation, and organic acid production. These problems did not occur or were less severe in the thermophilic BTF.

Since there is a lack of studies on the treatment of mixtures in thermophilic BTFs, looking at the treatment of single compounds may inform our knowledge. However, as Al-Faliti points out, studies by Duerschner (acetaldehyde at 24°C and 60°C) and Cox et al., (2001) (ethanol at 22°C and 53°C) — both studies on HAPs found in ethanol plant exhaust — show that we still do not know how temperature will affect the treatment of the ethanol plant exhaust. Duerschner found that elevated temperatures in the BTF negatively affected the removal of acetaldehyde due to the decrease in its solubility. Cox et al. found that ethanol was biodegraded effectively and at similar removal efficiencies for both ambient temperature and elevated temperatures. Al-Faliti found that both formaldehyde and methanol were degraded at high percentages in both columns. However, he also found that at lower concentrations the thermophilic column had a higher removal efficiency of formaldehyde than the mesophilic column and at higher concentrations the reverse was true. Thus, this study will shed light on the effect of thermophilic BTFs on the treatment of HAPs mixtures (mixtures of acetaldehyde, formaldehyde, ethanol, and methanol) that are found in ethanol plant exhaust.

## 2.5 Nutrient Solution Options

When a BTF is used, a nutrient solution needs to be introduced at some interval to keep the biofilm and microorganisms healthy and able to treat pollutants. The solution

adds moisture and nutrients to the column. In the studies mentioned above in Table 2.2 multiple different types and formulas were used to create nutrient solutions. This section goes over the recipes for the nutrient solutions used by these aforementioned studies.

Both Zehraoui et al. (2012) and Smith et al. (1998) used a composition of nutrient solution similar to Sorial et al. (1995). This nutrient solution was created to contain "the same amount (wt./wt.) of nutrient nitrogen (N) and phosphorous (P) for a given VOC loading (COD/N=50 and N/P=4)" (Smith et al., 1998). The buffer Smith et al. used maintained a BTF pH of 7.2 and was added at a rate of 20 L/day similar to Sorial et al. The solution used by Zehraoui et al. contained sodium bicarbonate, was at a pH of 7 and was supplied at a rate of 2.0 L/day. Sorial et al.'s nutrient solution maintained a pH of 7.7 +/- 0.2. The main components of Sorial et al's solution are listed in Table 2.3. In addition to the feed solution, a nutrient spike solution and a buffer solution were added. The nutrient spike solution (2M $NH_4C1$ and 0.22M $NaH_2PO_4 \cdot H_2O$) was added to the feed solution so that the COD-to-nitrogen ratio was 50:1; 1M $NaHCO_3$ was used as a pH buffer (the volume added depended on the volume of spike used) (Sorial et al., 1995). Nitrification inhibitor 2-chloro6(trichloromethyl)pyridine (TCMP) was also added.

Prado et al. (2008) used the nutrient solution laid out in Estévez et al. (2005). The solution was made up of three combined solutions: an aqueous-culture medium, a vitamin solution and a trace-mineral solution. The medium contained: 4.5 g/L $KH_2PO_4$, 0.5 g/L $K_2HPO_4$, 2.0 g/L $NH_4Cl$ and 0.1 g/L $MgSO_4 \cdot H_2O$. The vitamin solution was made up of: 0.2 g/L thiamine·HCl, 0.1 g/L riboflavin, 1.0 g/L nicotinic acid, 2.0 g/L Ca-pantothenate, 0.1 g/L biotin, 0.1 g/L thioctic acid, 0.1 g/L folic acid and 0.25 g/L pyridoxine HCl. Finally, the trace mineral solution contained: 120 mg/L $FeCl_3$, 50 mg/L $H_3BO_3$, 10 mg/L

$CuSO_4 \cdot 5H_2O$, 10 mg/L KI, 45 mg/L $MnSO_4 \cdot H_2O$, 20 mg/L $Na_2MoO_4 \cdot 2H_2O$, 75 mg/L $ZnSO_4 \cdot 7H_2O$, 50 mg/L $CoCl_2 \cdot 6H_2O$, 20 mg/L $AlK(SO_4)_2 \cdot 12H_2O$, 13.25 mg/L $CaCl_2 \cdot 2H_2O$ and 10,000 mg/L NaCl. The combined solution had a pH of 5.9, but this could be changed by adding NaOH or HCl (Estévez et al., 2005).

*Table 2.4-Nutrient Solution Feed Concentrations of Salts and Vitamins. Sorial et al. (1995)*

| **Component** | **Concentration, mg/L** |
|---|---|
| $B^{+3}$ | 0.0019 |
| $Ca^{+2}$ | 0.2682 |
| $Cl^{-1}$ | 2.0 |
| $Co^{+2}$ | 0.0104 |
| $CU^{+2}$ | 0.0112 |
| $Fe^{+3}$ | 0.0893 |
| $K^{+1}$ | 1.7316 |
| $Mg^{+2}$ | 0.431 |
| $Mn^{+2}$ | 0.0193 |
| $Mo^{+6}$ | 0.0166 |
| $NH_4^{+1}$ | 0.003 |
| $Na^{+1}$ | 0.002 |
| $SO_4^{-2}$ | 4.26 |
| $Zn^{+2}$ | 0.0231 |
| p-Aminobenzoic Acid | 0.0011 |
| Biotin | 0.0004 |
| Cyanocobalamin (B12) | 0.00002 |
| Folic Acid | 0.0004 |
| Nicotinic Acid | 0.0011 |
| Panothenic Acid | 0.0011 |
| Pyriodoxine Hydrochloride | 0.0023 |
| Riboflavin | 0.0011 |
| Thiamin Hydrochloride | 0.0011 |
| Thioctic Acid | 0.0011 |

Chen et al. (2010) used a nutrient solution made up of: 1.36 g/L $KH_2PO_4$, 5.68 g/L $Na_2HPO_4$, 3.96 g/L $(NH_4)_2SO_4$, 10.1 g/L $KNO_3$ and 1 mL/L of a trace element solution. The trace element solution consisted of: 50 g/L $MgSO_4 \cdot 7H_2O$, 14.7 g/L $CaCl_2 \cdot 2H_2O$, 2.86g/L $H_3BO_3$, 1.54 g/L $MnSO_4 \cdot H_2O$, 2.5 g/L $FeSO_4 \cdot 7H_2O$,0.027 g/L $CuCl_2 \cdot 2H_2O$,

0.044 g/L $ZnSO_4 \cdot 7H_2O$, 0.041 g/L$CoCl_2 \cdot 6H_2O$, 0.025 g/L $Na_2MoO_4 \cdot 2H_2O$, and 0.02 g/L$NiCl_2 \cdot 6H_2O$ (Song & Kinney, 2000). The solution has a pH of 7.3 and was recirculated every 3 days for 30 minutes.

Jamshidi et al. (2017) dosed the biofilter two times a day with a nutrient solution. It was made up of (g $L^{-1}$): 0.5 NaCl, 0.1 $NaHCO_3$, 0.15 $KH_2PO_4$, 0.3 $MgSO_4$, 0.01 g $FeSO_4$, 0.5 $NH_3SO_4$, 1.9 $ClNH_4$, 0.03 $MnSO_4$, and 0.03 $ZnSO_4$.

In the experiment done by Prado et al. (2004), 750 ml sludge was continuously recirculated through the BTF at a flow rate of 3.0 L/h, with no pH adjustment or nutrient addition.

In summary, almost every study has a slightly different nutrient solution formula. However, there are similarities between the different mixtures. Sorial et al., Smith et al., and Zehraoui et al. all followed the same recipe. It consisted of a feed solution, a nutrient spike solution, and a buffer solution. Estévez et al., and thus also Prado et al. (2008), used a solution made up of an aqueous culture medium, a vitamin solution, and a trace mineral solution. The use of HCl or NaOH was used to change the pH if needed. Chen et al. used a main nutrient solution with the addition of a trace element solution. Jamshidi et al. went back to a simpler nutrient solution. Thus, the main components of a nutrient solution, as defined by these studies, is a base nutrient feed solution with the additions of nutrients, vitamins, minerals, and a buffer solution if needed. The pH values for most of the solutions were between 7-8, except for Prado et al. (2008) which had a pH of 5.9.

# CHAPER 3: METHODS AND MATERIALS

## 3.1 Introduction

The material provided in this chapter describes in detail how the research was conducted in order to meet the research goals. The tests that were performed, the materials that were used, and the design of the experiments completed are outlined, listed, and portrayed in the following sections. Samples are followed from their point of origin — Nebraska ethanol plants — to the lab and through the testing process. This section discusses the methods used to test aqueous and gas samples from both ethanol plants and the BTF apparatus columns. The methods and experimental apparatus used to evaluate the effectiveness of using a bio-trickling filter (BTF) for ethanol plant exhaust treatment are also explained in detail in this chapter.

The aqueous sampling section looks at the different water purity tests that were completed on the ethanol- plant samples as well as the BTF nutrient solution influent and effluent. The gas sampling section focuses on the methods and machines used to look at the gaseous compounds in the aqueous samples from the ethanol plants; this section also analyzes the gas samples from different ports in the BTF columns.

## 3.2 Aqueous Sample Analysis

Samples from the first and second ethanol plant were tested for chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), and pH. The samples from the first ethanol plant where also tested for biological oxygen demand (BOD). The nutrient solution going through the BTF was tested for pH and nitrate. The liquid effluent from the BTF columns was tested for pH, COD, nitrate, total suspended solids (TSS), and

volatile suspended solids (VSS). The method used for each analysis is briefly described in the following sections.

### 3.2.1 Biological Oxygen Demand (BOD)

The BOD tests on the samples from the first ethanol plant were started as soon as the dilutions were performed. Dilutions were completed on the thin stillage and process-concentrate samples due to a visual inspection of high turbidity in these samples. Standard Methods: 5210B was used to test BOD for the samples (APHA, 2005). BOD bottles with volumes of 300 mL were used for each test. The dilution water was aerated overnight with the addition of nutrients and a nitrogen inhibitor. In order to determine the BOD of cooling tower water, $CO_2$ scrubber water, evaporator water, and rectifier column water, seeded samples of 25mL, 100mL, and 200mL were tested. The 1 mL seed in the bottles was taken from the aeration basin at the Theresa Street Wastewater Treatment Plant (Lincoln, NE) about 2 hours before the BOD tests were started and stored in a dark cool place until it was used. For thin stillage BOD tests, samples of 1:100 dilution at 3mL, 10 mL, and 25mL were tested. The process concentrate sample was tested at 1mL and 5mL undiluted and 50mL at 1:100 dilution all with the addition of 1ml seed. A sample consisting solely of dilution water with 1mL seed was also tested for calculation purposes.

### 3.2.2 Chemical Oxygen Demand (COD)

Hach TNT 820 (US EPA Reactor Digestion Method: 10211) was used to test each sample for COD (HACH, 2015). For testing of ethanol plant samples, the $CO_2$ scrubber sample was tested at ratios of 1:100. 1:200, 1:500, 1:1000, and 1:2000; evaporator water was tested at 1:100; rectifier column water was tested at 1:2; thin stillage was tested at

1:500, 1:1000, 1:2000, and 1:3000; and process concentrate was tested at 1:200 and 1:500 to obtain valid COD results. The COD in the influent nutrient solution and the effluent of both the mesophilic and thermophilic columns were measured. Dilutions between 1:10 and 1:50 were needed. Three tests were taken of each sample and the results are an average of these tests.

### 3.2.3 Total Nitrogen (TN)

Total nitrogen (TN) was tested using both Hach TNT 827 (Persulfate Digestion Method: 10208 (HR)) and Hach TNT 826 (Persulfate Digestion Method: 10208 (LR)) which are high range and low range measurement tests respectively (HACH, 2018a, 2018b). For testing of ethanol plant samples, the cooling tower water, evaporator water, and rectifier column water samples were tested undiluted. The thin stillage, process concentrate, and $CO_2$ scrubber were diluted to 1:500 1:100 and 1:100, respectively. Triplicate samples were averaged for results.

### 3.2.4 Total Phosphorus (TP)

Total phosphorus (TP) was tested using Hach TNT 844 (Ascorbic Acid Method: 10209/10210) (HACH, 2016). This is the same method as EPA 365.1, 365.3. Ethanol plant water samples, cooling tower water, $CO_2$ scrubber water, evaporator water, and rectifier column water were tested undiluted; thin stillage was diluted to 1:500; process concentrate was diluted to 1:100. Triplicate samples were tested.

### 3.2.5 pH

The pH of each sample was tested using a Thermo Scientific Orion 4 Star pH meter. This method was used for both ethanol plant samples and both the effluent and influent from the BTF columns. Samples of centrifuged thin stillage and process

concentration were also tested. Each test was done three times and the results were averaged.

### 3.2.6 Suspended Solids

The total suspended solids (TSS) and volatile suspended solids (VSS) for each sample were tested using the method outlined by Standard Methods 2540D (APHA, 2005). For testing of ethanol plant samples, a volume of 20mL was filtered for cooling tower water, $CO_2$ scrubber water, evaporator water, and rectifier column water, 1mL of thin stillage, and 10mL of process concentrate. For influent and effluent samples from the BTF, 200 ml samples were used. Three tests were done for each sample and the results were averaged.

### 3.2.7 Nitrate

Nitrate was measured for both the influent and effluent from the BTF. Samples were stored at 4$^{o}$C until testing. During storage, the pH of the samples was lowered to below 2 using HCl and before sampling the pH was raised back up to around 7 using NaOH. Hach TNT 836 (Dimethylphenol Method: 10206) was used to measure triplicate tests of each sample (HACH, 2021).

## 3.3 Gas Sample Analysis

Gas sampling was completed for two different projects. The first was for analyzing the gaseous compounds in aqueous streams within an ethanol plant. The second used different sampling machines to identify the type and amount of different gaseous compounds in the effluent of different ports on bio-trickling filter columns.

### 3.3.1 Solid Phase Extraction (VASE)

Vacuum-assisted sorbent extraction (VASE) method, in conjunction with a gas chromatography/mass spectrometry (GC/MS), was used to analyze gaseous compounds in aqueous streams within an ethanol plant. First, 2 mL of aqueous sample was placed in a 20 mL glass vial. A VASE pin was inserted into the vial, the vial was put under a vacuum of 30 mmHg, and the vacuum was checked before moving forward. The vacuum applied allows for VOCs in the headspace of the vial to be adsorbed by the pin. The sample was then placed in a 5600 SPES Sorbent Extraction System for a period of three hours at 70°C and 200 rpm. After incubation, the samples were placed in a cold tray for a period of 10 minutes before the pins were extracted from the vials and placed in sleeves for safe keeping. Triplicate pins were run for each sample. VASE pin samples were then inserted into the GC/MS for analysis. This method was used to determine the concentrations of acetaldehyde, ethanol, methanol, n-propanol, and acetal in the samples.

### 3.3.2 Gas Chromatography/Mass Spectrometry (GC/MS)

Acetaldehyde, ethanol, and methanol concentrations from different ports in the bio-trickling filter apparatus columns were measured using an Agilent 7820A GC system with a Mass Spectrometry (MS) detector and 30 m, 0.25 mm I.D. HP-5MS column. The GC was operated in ‘1:10 split mode’ with an inlet temperature of 250 °C and an isothermal oven temperature of 30 °C. Helium at a flow rate of 1mL/min was used as the carrier gas. The injection valve was maintained at 80 °C and contained a 0.25 mL loop. A run time of three minutes was sufficient to meet the retention time for each compound being measured under these conditions. Three replicates were completed for each sample.

### 3.3.3 Fourier-Transform Infrared (FTIR) Spectrometer

In order to determine the concentration of formaldehyde gas at different ports, a Nicolet IS20 Fourier-transform infrared (FTIR) spectrometer, obtained from ThermoFisher, was used. The FTIR was equipped with a 2-meter gas cell with a volume of 200 mL and was kept at a temperature of 161°C to avoid condensation in the walls. Nitrogen gas was used to constantly purge the instrument to eliminate any condensation in the instrument or in the gas cell during use. A resolution of 0.5-1 cm was chosen to provide a high measurement resolution. To ensure high sensitivity and to eliminate noise associated with sample spectrum, a 64-scans procedure was chosen.

To obtain a representative measure of the concentration of formaldehyde at a port, each sample was allowed to run through the 200 mL gas cell flowing at 1 L/min for 10 minutes. Next, the inlet and outlet valves of the gas cell were closed for 5 minutes to stabilize the sample temperature inside the gas cell for better detection of the formaldehyde and to avoid condensation along the walls of the gas cell. After 5 minutes had passed, the measurement of the sample was finally taken. The wavelength range used for detection of the formaldehyde spectrum was determined to be between 2657.0-2784.0 $cm^{-1}$.

Measurements were taken at Ports 1, 2, 3, 6, 11, 12, 13, and 16. Two replicates were completed at each port with the exception of one replicate at Ports 6 and 16. Sampling of the ports for VOC concentration was completed three times a week.

### 3.3.4 Micro Gas Chromatograph (microGC)

In order to detect $CO_2$ at the top and bottom of the (BTF) columns, an Agilent Technologies 490 Micro Gas Chromatograph (microGC) with a thermal conductivity

detector and a two-channel module was used. The sample inline temperature for both channels was 35 °C and the injection pump run time was 5 seconds. The first channel contained a 10 m MS5A heated injector maintained at 60 °C with a channel temperature of 75°C and detected $N_2$ and $O_2$. The second channel contained a 4m PPQ module with an injector temperature of 50 °C and a column temperature of 55 °C and detected the amount of $CO_2$.

## 3.4 Characterization of Ethanol Plant Streams

The plant operation of a dry-mill ethanol plant is briefly explained in Section 1.1.1. This section provided more detail related to the steams is provided below. The samples that were collected, the collection procedure, and the sample dilutions are listed in the sections below.

### 3.4.1 Description of Ethanol Plant Streams

A process flow diagram representative of most US dry-mill ethanol plants is presented in Figure 3.1. This diagram is representative of the two plants where samples were collected for the studies in this thesis. A total of 6 samples were taken from the first plant and 17 samples were collected from the second ethanol plant. The first plant follows the process flow of the grey and black lines in the above diagram, whereas the second plant flows the blue and black process lines.

The samples taken from the first plant were from the cooling tower (CT), recycled water from the $CO_2$ scrubber ($CO_2$) (Stream 17), evaporator water (EV) (Stream 13), condenser water (RC), thin stillage (TS) (Stream 9, 10, or 11), and process concentrate (PC).

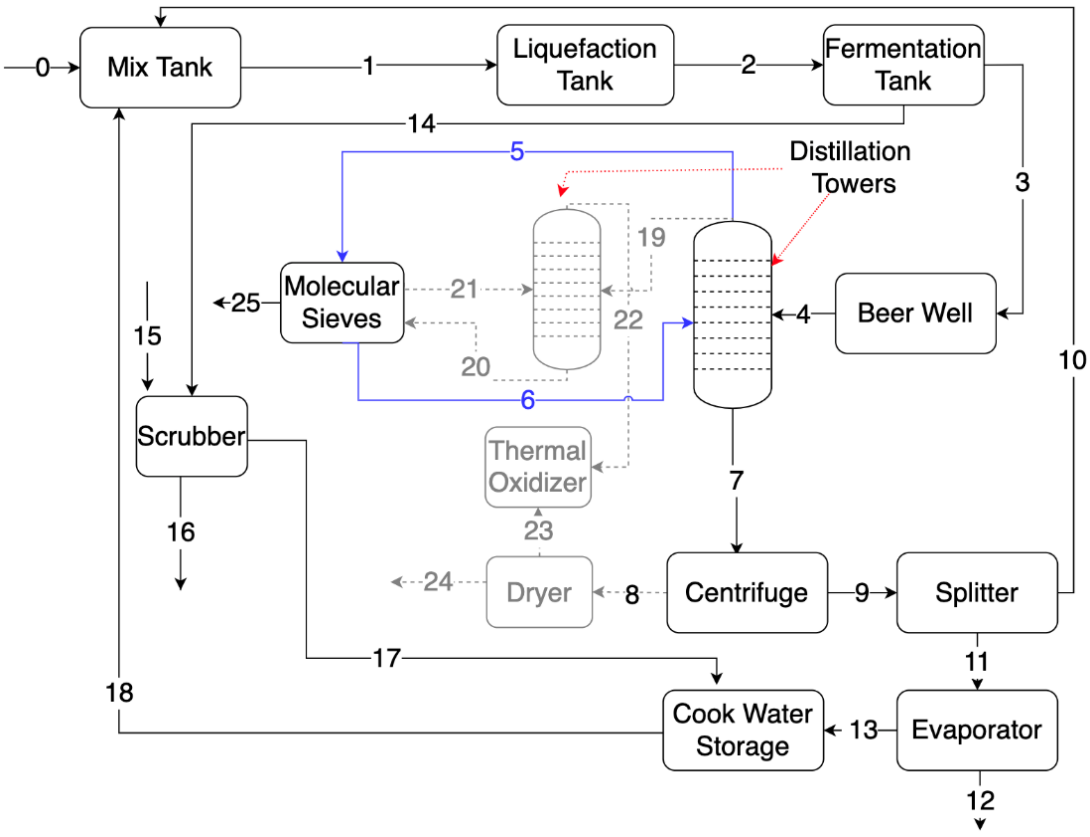



*Figure 3.1-Ethanol Plant Flow Diagram with Streams Labelled*

The locations of the samples taken from the second plant are as follows. Mix Tank Mash and Liquefaction Tank Mash represents the composition of the mash in Streams 1 and 2, respectively. Fermentation Tank Beer and Beer Well Beer represents the composition of the beer in Streams 3 and 4, respectively. Column Tops represents the composition of the distillation tops in Stream 5. Mole-Sieve Reject represents the composition of ethanol-water solution rejected from the molecular sieves in Stream 6. Column Bottoms represents the composition of distillation column bottoms in Stream 7. Solids represents the composition of the wet cake in Stream 8. Thin stillage represents the compositions of Streams 9, 10, and 11. Corn Oil/Corn Syrup represents the composition of Stream 12. Evaporated Water represents the composition of the evaporator water of

Stream 13. Water 15 represents the composition of the well-water in Stream 15. $CO_2$ Scrubber Water represents the composition of the water coming from the $CO_2$ scrubber in Stream 17. Recycled Cook Water refers to the composition of the water in Stream 18. The RO Reject (RC) refers to the water removed from the reverse osmosis system and is not listed in the diagram. The Cooling Tower Blow Down (CT), also not in the diagram, refers to the water removed from the cooling towers. These two streams are later combined into the Cooling Tower Blow Down + RO Reject stream (PC) also not listed in the figure above.

The second ethanol plant omits the use of a thermal oxidizer and a second distillation tower and only uses a molecular sieve for further treatment of ethanol after initial distillation. After distillation, the tops (5) are sent to molecular sieves. Within the molecular sieves, a water-ethanol mixture flows through very small beads. The smaller ethanol molecules pass through the beads while the larger water molecules are retained. High purity ethanol exits the molecular sieves (25) and a water-ethanol mixture is recycled back to the distillation tower (6).

The first ethanol plant follows a slightly different process. The tops of the first distillation tower are sent to another distillation tower (19). In this tower, the volatile impurities such as methanol and acetaldehyde are removed from the ethanol-water solution and sent to a thermal oxidizer (22) where they are combusted, releasing more HAPs. The bottom portion of the column (20) is sent to the molecular sieve. The bottom portion of the first column (7) is sent to a centrifuge where the solids are removed (8). The solids are then dried, and the vapors are (23) again sent to a thermal oxidizer. The thin stillage (9) is sent to a splitter where a portion (10) is sent back to the mixing tank.

The remainder (11) is sent to an evaporator where water is removed (13) and sent to the cook water storage. The resulting liquid is corn oil and corn syrup.

### 3.4.2 Ethanol Plant Sample Collection

Samples from both ethanol plants followed the same sample collection methods. Samples were taken directly from the ethanol plant streams and placed in 1L plastic bottles. No headspace was allowed in the sampling bottles. These bottles were placed in coolers with dry ice to keep the samples at 4$^{o}$ C while they were being transferred back to the lab. Once at the lab, the samples were placed in a refrigerator until testing could commence.

## 3.5 Operation of the Bio-Trickling Filter (BTF)

This section details the design of the BTF. The lab-scale BTF is made up of multiple parts including the columns, gas delivery system, nutrient delivery system, and sampling set-up. Each part is necessary for bacterial growth, exhaust treatment, and testing of varying levels of treated samples.

### 3.5.1 Column Design

A schematic of the experimental apparatus is provided in Figure 3.2. The apparatus is made up of two BTFs that operate in parallel. Each BTF consists of a three-inch internal- diameter glass column that contains media. This media consists of (0.3” - 0.5”) pellets of diatomaceous earth (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA) that are mainly $SiO_2$ with a significant fraction of $Al_2O_3$. They have a mean pore diameter of 20 μm, BET surface area of 0.27 m2/g,[3] and a bed density of 513 kg/m (Catalyt Carrier, personal communication, April 2, 2003). These physical properties and others can be found in the brochure in Appendix E.

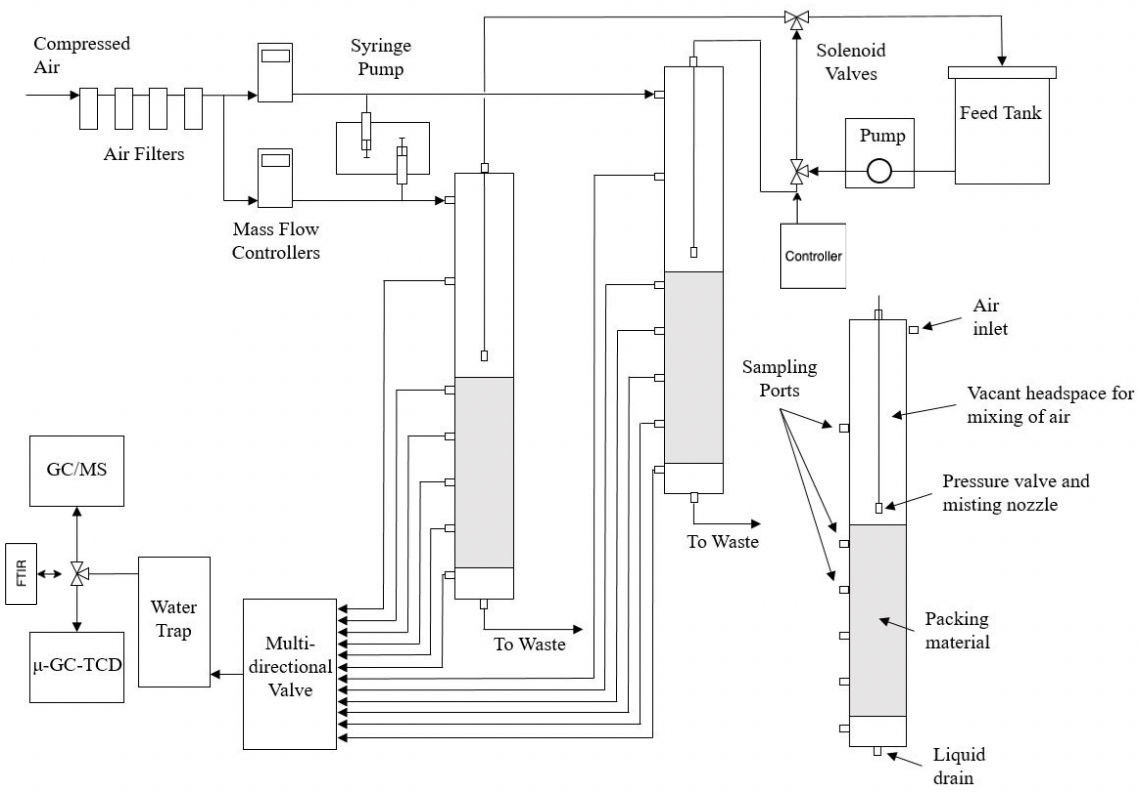



*Figure 3.2-Schematic of Experimental Apparatus*

The first BTF column was operated at room temperature, 21°C, and can be referred to as the mesophilic column. The second column was operated at 60°C and is referred to as the thermophilic BTF. In order to elevate the temperature of the thermophilic column, heating tape was wrapped around the outside of the column, covering approximately half of the outside surface area of the column and a BriskHeat X2-120JTP Single Zone PID Temperature controller was used to control the temperature.

Along each column there are airtight sampling ports located at packed depths of 1.5 (3.81 cm), 11.5 (29.2 cm), 21.5 (54.6 cm), 31.5 (80.0 cm), and 37.5 inches (95.2 cm). The first sampling port is located 21.0 inches (53.3 cm) from both the top of the pacing material and below the gas inlet. The placement of a thermocouple in the port at 21.5

inches (54.6 cm) in the thermophilic column allows for temperature control of the column.

The media in the columns is referred to as the bed of the BTF. Before the project started, both beds were seeded with microorganisms. The mesophilic BTF bed was submerged overnight in return activated sludge obtained from the local wastewater treatment plant (WWTP), while the thermophilic bed was submerged overnight with cooking compost slurry. The compost was taken from yard waste from the center of a windrow, and then it was mixed with water to create the slurry. Two g/L of glucose was added to both BTFs overnight. Afterwards, both BTFs were used for the degradation of acetaldehyde and formaldehyde (Al-Faliti, 2020; Duerschner, 2019).

### 3.5.2 Gas Delivery System

House air is filtered through a Parker Filtration 2000 series compressed air apparatus, a Balston sterile air filter, and finally a Parker compressed air-gas-water separator. Following filtration, the air stream is split into two streams, and flowrate is regulated to 8 L/min (which corresponds to an EBRT of 32 seconds) by two Aalborg mass-flow controllers (Orangeburg, New York). A mixture made up of acetaldehyde, formalin (contains 37% formaldehyde by weight and 10-15% of methanol as a stabilizer), and ethanol, diluted to a known amount with DI water, is then infused into the air stream through a septum housed in a stainless-steel tee union. A Harvard Apparatus Pump 11 Elite syringe pump (Holliston, MA) and Hamilton Gastight syringes (Reno, NV) were used to regulate the infusion. Finally, the air stream is injected into the top of the column, 42 inches (106.7 cm) above the packing material, which allows the mixture-laden air to uniformly mix before diffusing into the bed.

### 3.5.3 Nutrient Delivery System

A nutrient/buffer solution (trickling fluid) is delivered to the BTF beds intermittently via a Cole Parmer cavity-style pump head that is equipped with a variable speed pump and timer-controlled solenoid valves. The nutrient solution consists of essential inorganic salts and vitamins necessary to grow microorganisms and is only sent through the column once. The solution is prepared in five-gallon batches that usually last two weeks. A pressure valve and a misting nozzle, located 4 inches (10.2 cm) above the packing material, control the pipe delivering the solution to the BTF. The valve is opened for 2.5 seconds on a 1-minute cycle controlled by the timer. The composition of the nutrient solution is similar to other solutions created for the same purpose (Sorial et al., 1997). A detailed description of the components of the nutrient solution is provided in Appendix B.

### 3.5.4 Nutrient Delivery System Controller

The nutrient solution flow through the solenoids is controlled by an Arduino controller. A computer cord supplies a 120V current to the controller box. Just inside the box is a plug that receives the 120V. A 120V to 5V exchanger takes power from the plug and connects with the Arduino board. The board is programed to run two circuits. The first circuit is on for 2.5 seconds. Next, both are turned off 2 seconds. Then, the second circuit is on for 2.5 seconds. Finally, they are both off for 53 seconds. This minute-long program is run on a loop. The two circuits both attach to a relay board where power from the 120 V box is also connected. Wires then run to a plug that interfaces on the outside of the box. The two solenoid valves are plugged into the control box and thus are

controlled by the turning off and on of the power by the Arduino. A diagram and picture of the controller can be found in Appendix C.

### 3.5.5 Sampling Set-Up

Using a multidirectional valve and controller, gas samples can be taken at each of the ports along the BTF columns. The samples pass through a water trap and from there a series of one-way values can direct the gas sample to either a Nicolet IS20 FTIR spectrometer (FTIR), an Agilent Technologies 490 Micro Gas Chromatograph (microGC) with a thermal conductivity detector, or an Agilent 7820A GC system with a Mass Spectrometry (MS) detector (GC/MS). The exhaust gas from the GCs is let into the atmosphere, while the exhaust gas from the FTIR is run through a bucket of activated carbon.

# CHAPER 4: BIOFILTRATION OF SYNTHETIC ETHANOL PLANT EXHAUST MIXTURES WITH INCREASING ETHANOL CONCENTRATIONS UNDER MESOPHILIC AND THERMOPHILIC CONDITIONS

## 4.1 Introduction

Ethanol in the United States (US) is a biofuel produced primarily (97%) from the fermentation of corn in dry-mill ethanol plants (82%) (Eidman, 2007). Due to the 1973 oil embargo by Arab members of the Organization of Petroleum Exporting Countries (OPEC), an increase in the percentage of ethanol found in gasoline rose throughout the late 1970s and early 1980s to compensate for the reduced oil supply (Office of the Historian, 2016). This geopolitical situation caused policies and programs run by both the state and federal governments to create incentives for using ethanol in gasoline (US Energy Information Administration, 2020). Even though a major tax credit was removed in 2011, consumption of ethanol in the US has continued to rise from about 2 million gallons in 1981 to about 14.5 billion gallons in 2019. In part, this increase is due to ethanol replacing methyl tertiary butyl ether (MTBE) in gasoline. It is also due to the renewable fuel standard (RFS) under the Energy Independence and Security Act of 2007 (EISA) (US Energy Information Administration, 2020) that requires that 36 billion gallons of renewable fuel be blended into transportation fuel by 2022 (US EPA, 2017).

As of May 2021, there are 202 ethanol plants in the United States that have a total capacity to produce 17,468 MMgal/yr of ethanol (BBI International, 2021). Figure 4.1

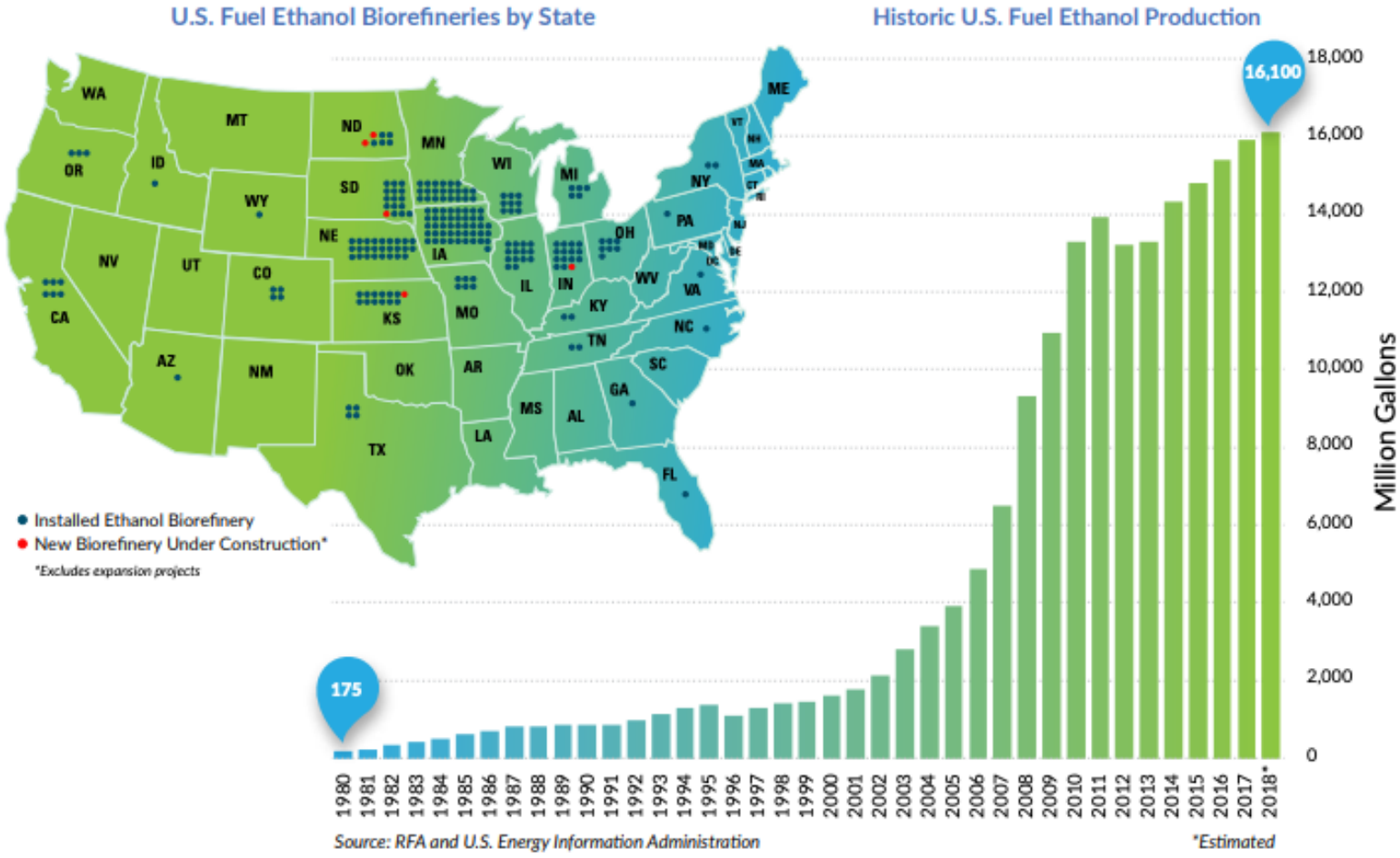



*Figure 4.1-Locations and Numbers of Ethanol Plants by State. Graph of Increase in Ethanol Production Over Time (Renewable Fuels Association, 2019).*

from the article “Powered with Renewed Energy” by the Renewable Fuels Association (RFA) (2019) gives a visual representation of the location of the ethanol plants in the US, as well as the relative increase in ethanol production from 1980 until 2018.

However, during the production of ethanol, volatile organic compounds (VOCs) are released. Some of the compounds in the ethanol plant exhaust include acetaldehyde, formaldehyde, acrolein, methanol, ethanol, and acetic acid (Brady & Pratt, 2007). Furthermore, some of these VOCs are listed on the US Environmental Protection Agency’s (EPA) list of hazardous air pollutants (HAPs) (US EPA, 2015). The EPA regulates the quantity of HAPs each plant is allowed to release into the environment (US EPA, 2021).

The industry standards for treating HAPs from ethanol plant exhaust are $CO_2$ scrubbers and regenerative thermal oxidizers (RTOs) (Brady & Pratt, 2007). $CO_2$ scrubbers are currently being used to remove the HAPs from the air exiting the fermenters. The process depends on water to dissolve volatile HAPs back into the liquid stream instead of the gaseous state. The water is subsequently recycled back into the fermenter. The rest of the gas, which is composed mostly of $CO_2$, is released into the atmosphere. Thermal oxidizers are another alternative equipment that is used to treat HAPs. After ethanol is removed from the fermented solution, part of the remaining material is called thin stillage. In order to improve the shelf life — and for transportation to farms for cattle feed — the thin stillage is further dried. During the drying process, more volatile HAPs are released. The off-gas from the dryer is treated with an RTO. The RTO uses natural gas to burn the HAPs in the off-gas (Bryan, 2003).

Ethanol plant emissions data from upstream of tradition treatment methods are rare. A study by Chen et al. (2010) reported effluent concentration of acetaldehyde and formaldehyde from a dryer to be 20.7 and 16.4 $ppm_v$ with Henry's Law Constant ($L_{liquid}/L_{gas}$) equals to $4x10^{-3}$ and 6.8 $x10^{-6}$, respectively. Plant A preformed emission testing in 2006 and the results are shown in Table 4.1. Finally, the HAP concentrations from effluent from a scrubber, that had dryer exhaust as an influent, were measured in an ethanol plant in Columbus, NE (Aly Hassan). These values and the actual main HAP constituent values from before the scrubber, if the scrubber operated at an optimistic 90% removal efficiency are listed in Table 4.2. The typical amount of VOCs from a dryer is 70.4 kg/day on average (Aly Hassan, 2018).

*Table 4.1-Characteristics of Gaseous HAPs Streams at Pacific Ethanol East Plant (Aly Hassan, 2018)*

| | Pre-Fermenter Scrubber | $CO_2$ Scrubber | Dryer RTO |
|---|---|---|---|
| Stack Volumetric Flow Rate, acfm | 1,144 | 1,390 | 60,074 |
| VOC, $ppm_v$ | 5,397 | 7,565 | 305.4 |
| Ethanol, $ppm_v$ | 11,548 | 15,321 | - |
| Acetaldehyde, $ppm_v$ | 35.7 | 25.2 | - |

*Table 4.2- Actual and Before Scrubber Estimates of HAPs Concentrations Out of an Ethanol Plant in Columbus, NE (Aly Hassan, 2018)*

| Constituent | Concentration, $ppm_v$ | | | | |
|---|---|---|---|---|---|
| | Test 1 | Test 2 | Test 3 | Average | Before Scrubber |
| Acetaldehyde | 2.75 | 2.49 | 3.14 | 2.79 | 27.9 |
| Acetic Acid | 0.85 | 0.53 | 0.53 | 0.64 | - |
| Acrolein | 2.43 | 2.36 | 1.75 | 2.18 | 21.8 |
| Ethanol | 27.7 | 24.0 | 21.1 | 24.3 | 243 |
| Ethyl Acetate | < 0.41 | < 0.41 | < 0.41 | < 0.41 | - |
| Formaldehyde | < 1.75 | < 1.75 | < 1.75 | < 1.75 | 17.2 |
| Formic Acid | < 0.32 | < 0.32 | < 0.32 | < 0.32 | - |
| Methanol | < 0.52 | < 0.48 | 1.26 | < 0.75 | 7.5 |

Due to the fact that these processes use either a significant amount of water or energy (natural gas) to operate, the utilization of a bio-trickling filter (BTF) is proposed as an innovative industrial HAPs treatment method (Chen et al., 2010). BTFs are made up of: a column, media to support microbial growth, microbial seed, a gas stream that contains oxygen, and a nutrient stream to feed the microbes (Delhoménie & Heitz, 2005). BTFs use less water (about 0.5% of the amount needed for a $CO_2$ scrubber) and energy (no natural gas) than $CO_2$ scrubbers and RTOs.

This study looks at the treatment of a synthetic ethanol plant stream using a BTF under mesophilic (21°C) and thermophilic (60°C) conditions. The synthetic stream is made up of a mixture of acetaldehyde, formaldehyde, and methanol with the addition of different amounts of ethanol to produce two different mixtures. While the amount of HAPs in an ethanol plant stream are more consistent, the percentage of ethanol can vary depending on the fermenter conditions. A bioscrubber can also affect the amount of ethanol in an ethanol plant exhaust stream. Therefore, this study will look at the treatment of HAPs, in concentrations similar to ethanol plant exhaust, by using a BTF under both mesophilic and thermophilic conditions. It will also look at the effect of two concentrations of ethanol on the treatment of the mixture.

## 4.2 Materials and Methods

This section discusses the methods for testing aqueous and gas samples from the BTF. It also explains the design and components of the BTF. Finally, it goes over the HAP mixture composition and amount of ethanol in both mixtures.

### 4.2.1 Aqueous Sampling

Chemical oxygen demand (COD) was tested using the Hach TNT 820 (US EPA Reactor Digestion Method: 10211) method (HACH, 2015). The COD in the influent nutrient solution and the effluent of both the mesophilic and thermophilic columns were measured. Dilutions between 1:10 and 1:50 were needed to be in the range of the test. Triplicate tests were completed for each sample and the results are an average of these three.

The total suspended solids (TSS) for each sample were tested using the method outlined by Standard Methods 2540D (APHA, 2005). For influent and effluent samples from the BTF, 200 ml samples were used. Three tests per sample were averaged for the result. The pH of each sample was tested using a Thermo Scientific Orion 4 Star pH meter. This method was used on both the effluent and influent from the BTF columns. Each sample was measured three times and the result is the average of these measurements.

### 4.2.2 Gas Sample Analysis

Acetaldehyde, ethanol, and methanol concentrations from different ports in the BTF apparatus columns were measured using an Agilent 7820A GC system with a Mass Spectrometry (MS) detector and 30 m, 0.25 mm I.D. HP-5MS column. The GC was operated in ‘1:10 split mode’ with an inlet temperature of 250 °C and an isothermal oven temperature of 30 °C. Helium at a flow rate of 1mL/min was used as the carrier gas. The injection valve was maintained at 80 °C and contained a 0.25 mL loop. A run time of three minutes was sufficient to meet the retention time for each compound being measured under these conditions. Three replicates were completed for each sample.

In order to determine the concentration of formaldehyde gas at different ports, a Nicolet IS20 Fourier-transform infrared (FTIR) spectrometer obtained from ThermoFisher was used. The FTIR was equipped with a 2-meter gas cell with a volume of 200 mL and was kept at a temperature of 161°C to avoid condensation in the walls. Nitrogen gas was used to constantly purge the instrument to eliminate any condensation in the instrument or in the gas cell during use. A resolution of 0.5-1 cm was chosen to provide a high measurement resolution. To ensure high sensitivity and to eliminate noise associated with sample spectrum, a 64-scans procedure was chosen based on the recommendation of a ThermoFisher technician.

In order to obtain a representative measure of the concentration of formaldehyde at a port, each sample was allowed to run through the 200 mL gas cell flowing at 1 L/min for 10 minutes. Next, the inlet and outlet valves of the gas cell were closed for 5 minutes to stabilize the sample temperature inside the gas cell for better detection of the formaldehyde and to avoid condensation along the walls of the gas cell. After five minutes, the measurement of the sample was finally taken. The wavelength range used for detection of the formaldehyde spectrum was determined to be between 2657.0-2784.0 $cm^{-1}$.

Measurements were taken from the port above the media, the next two ports (both in the media), and finally at the last port on the column below the media for the ports along both columns. Two replicates were completed at each port with the exception of one replicate at the bottom ports. Sampling of the ports for VOC concentration was completed three times per week.

### 4.2.3 Bio-Trickling Filter and Column Design

This section details the design of the BTF. The lab-scale BTF is made up of multiple parts including the columns, gas delivery system, nutrient delivery system, and sampling set-up. Each part is necessary for bacterial growth, exhaust treatment, and testing of varying levels of treated samples.

A schematic of the experimental apparatus is provided in Figure 4.2. The apparatus is made up of two BTFs that operate in parallel. Each BTF consists of a three-inch internal diameter glass column that contains media. This media consists of (0.3" - 0.5") pellets of diatomaceous earth (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA) that are mainly $SiO_2$ with a significant fraction of $Al_2O_3$. They have a mean pore diameter of 20 μm, BET surface area of 0.27 m2/g,[3] and a bed density of 513 kg/m (Catalyt Carrier, personal communication, April 2, 2003). These physical properties and others can be found in the brochure in Appendix E.

The first BTF column was operated at room temperature (21°C) and can be referred to as the mesophilic column. The second column was operated at 60°C and is referred to as the thermophilic BTF. In order to elevate the temperature of the thermophilic column, heating tape was wrapped around the outside of the column, covering approximately half of the outside surface area of the column and a BriskHeat X2-120JTP Single Zone PID Temperature controller was used to control the temperature.

Along each column there are airtight sampling ports located at packed depths of 1.5 (3.81 cm), 11.5 (29.2 cm), 21.5 (54.6 cm), 31.5 (80.0 cm), and 37.5 inches (95.2 cm). The first sampling port is located 21.0 inches (53.3 cm) from both the top of the pacing material and below the gas inlet. The placement of a thermocouple in the port at 21.5

inches (54.6 cm) in the thermophilic column allows for temperature control of the column.

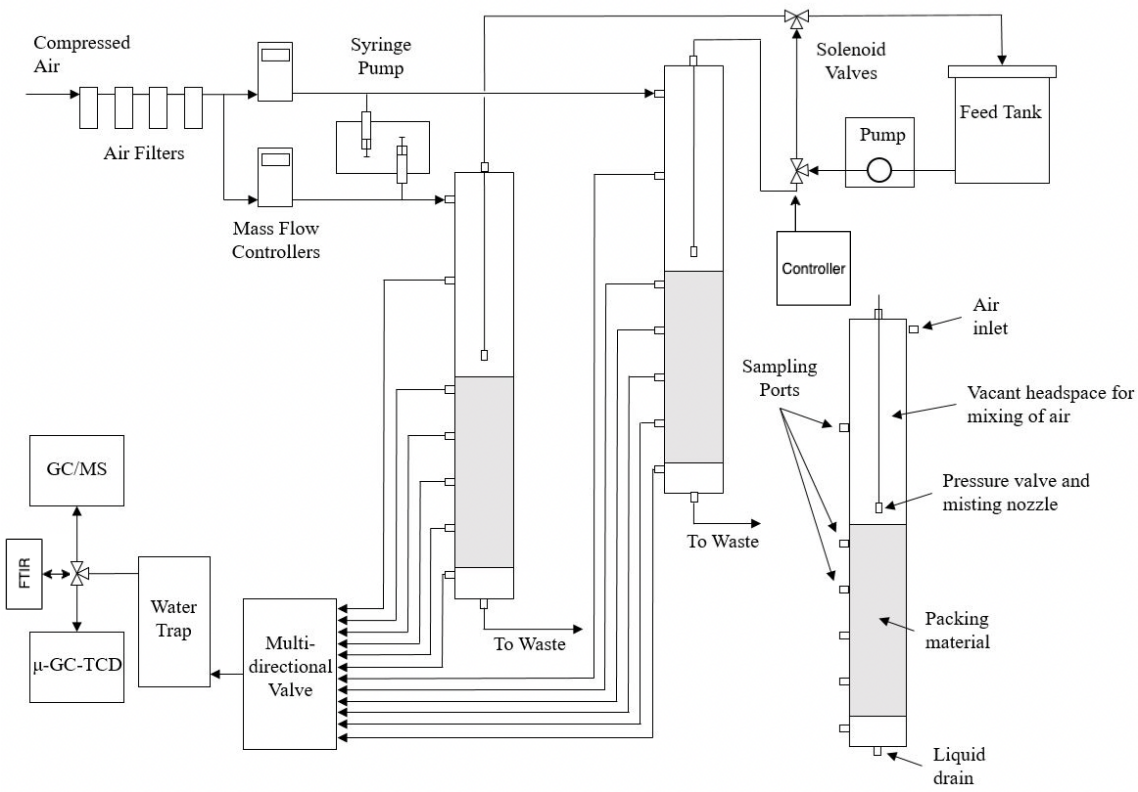



*Figure 4.2-Schematic of Experimental Apparatus*

The media in the columns is referred to as the bed of the BTF. Before the project started both beds were seeded with microorganisms. The mesophilic BTF bed was submerged overnight in return-activated sludge obtained from the local wastewater treatment plant (WWTP), while the thermophilic bed was submerged overnight with cooking-compost slurry. The compost was taken from yard waste from the center of a windrow, and then it was mixed with water to create the slurry. Two g/L of glucose were added to both BTFs overnight. Afterwards, both BTFs were used for the degradation of acetaldehyde and formaldehyde (Al-Faliti, 2020; Duerschner, 2019).

### 4.2.4 Gas Delivery System

House air is filtered through a Parker Filtration 2000 series compressed air apparatus, a Balston sterile air filter, and finally a Parker compressed air-gas-water separator. Following filtration, the air stream is split into two streams, and flowrate is regulated to 8 L/min (corresponds to an EBRT of 32 seconds) by two Aalborg mass flow controllers (Orangeburg, New York). A mixture made up of acetaldehyde, formalin (contains 37% formaldehyde by weight and 10-15% of methanol as a stabilizer), and ethanol — diluted to a known amount with DI water — is then infused into the air stream through a septum housed in a stainless-steel tee union. A Harvard Apparatus Pump 11 Elite syringe pump (Holliston, MA) and Hamilton Gastight syringes (Reno, NV) were used to regulate the infusion. Finally, the air stream is injected into the top the column, 42 inches (106.7 cm) above the packing material, allowing the mixture-laden air to uniformly mix before entering the bed.

### 4.2.5 Nutrient Delivery System

A nutrient buffer solution (trickling fluid) is delivered to the BTF beds intermittently via a Cole Parmer cavity-style pump head equipped with a variable speed pump and timer-controlled solenoid valves. The nutrient solution consists of essential inorganic salts and vitamins necessary to grow microorganisms and is only sent through the column once. The solution is prepared in five-gallon batches that usually last two weeks. A pressure valve and a misting nozzle — located 4 inches (10.2 cm) above the packing material — control the pipe delivering the solution to the BTF. The valve is opened for 2.5 seconds on a 1-minute cycle controlled by the timer. The composition of the nutrient solution is similar to other solutions created for the same purpose (Sorial et

al., 1997). A detailed description of the components of the nutrient solution is provided in Appendix B.

The nutrient solution flow through the solenoids is controlled by an Arduino controller. A computer cord supplies a 120V current to the controller box. Just inside the box is a plug that receives the 120V. A 120V to 5V exchanger takes power from the plug and connects with the Arduino board. The first circuit is on for 2.5 seconds. Next, both are turned off 2 seconds. Then, the second circuit is on for 2.5 seconds. Finally, they are both off for 53 seconds. This minute-long program is run on a loop. The two circuits both attach to a relay board where power from the 120V box is also connected. Wires then run to a plug that interfaces with the outside of the box. The two solenoid valves are plugged into the control box and thus are controlled by the turning off and on of the power by the Arduino. A diagram and picture of the controller can be found in Appendix C.

### 4.2.6 Sampling Setup

Using a multidirectional valve and controller, gas samples can be taken at each of the ports along the BTF columns. From there the gas sample can be directed to either a Nicolet IS20 FTIR spectrometer (FTIR), an Agilent Technologies 490 Micro Gas Chromatograph (microGC) with a thermal conductivity detector, or an Agilent 7820A GC system with a Mass Spectrometry (MS) detector (GC/MS). The exhaust gas from the GCs is let into the atmosphere, while the exhaust gas from the FTIR is run through a bucket of activated carbon.

### 4.2.7 Mixture Make-ups

Two different formulas/mixtures were tested, and the composition of each is listed in Table 4.1. The amount of HAPs were the same in each mixture. However, the ethanol

concentration was increased from 50 ppm to 100 ppm between the two mixtures. The mixtures were tested in both a mesophilic (21ºC) and a thermophilic (60ºC) column. These temperature conditions are comparable to that of ethanol plant exhaust streams leaving the fermentation tanks and dryers, respectively. Aqueous effluent samples were also taken and analyzed to help understand the environment inside the columns.

*Table 4.3-Mixture Make-up of Synthetic Ethanol Plant Exhausts*

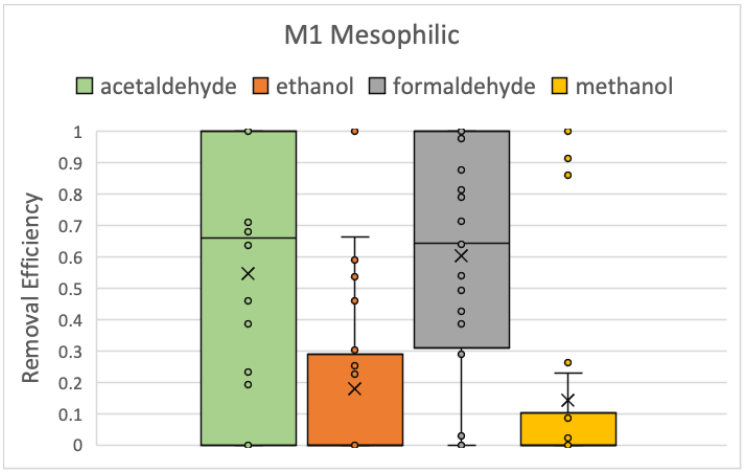
| Compounds | Mixture 1 (ppm) | Mixture 2 (ppm) |
|---|---|---|
| Ethanol | 50 | 100 |
| Acetaldehyde | 100 | 100 |
| Formaldehyde | 50 | 50 |
| Methanol | 13.5 | 13.5 |

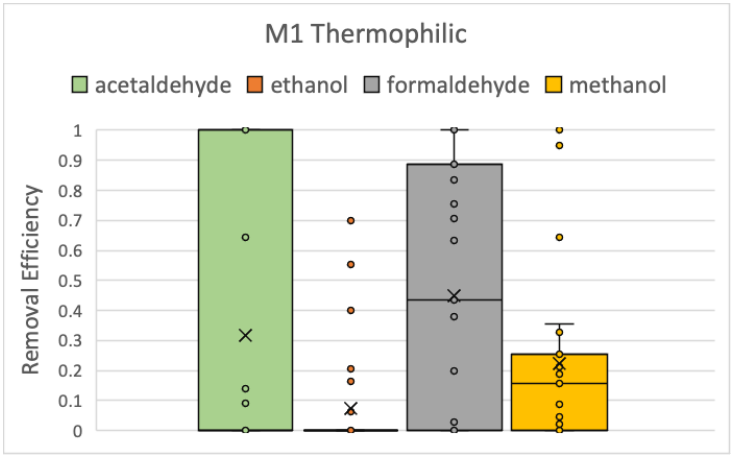
## 4.3 Results

The results from this study will compare the treatment of a HAPs mixture with two different ethanol concentrations that is similar to ethanol plant exhaust. Results will further compare the effect of temperature on the treatment of each mixture. The analysis of effluent samples for COD, TSS, and pH help explain the processes that are taking place within each column.

### 4.3.1 Biodegradation of Mixtures

This study looks at the use of a BTF to treat a synthetic HAPs mixture with different ethanol concentrations that has a similar composition to ethanol plant exhaust. The make-up of Mixture 1 (HAPs with 50 ppm ethanol) and 2 (HAPs with 100 ppm ethanol) are listed in Table 4.1. The two mixtures were also treated under mesophilic and thermophilic conditions. Figures 4.3 and 4.4 show the removal efficiency of each of the VOCs in Mixture 1 under mesophilic and thermophilic conditions.




The removal efficiency of aldehydes and alcohols, except methanol, is higher in the mesophilic column compared to the thermophilic column for Mixture 1. Ethanol removal efficiency is low, as is methanol removal, for both conditions. Formaldehyde has the highest removal efficiency average between the two conditions.

In Figures 4.5 and 4.6, it is apparent that, similar to Mixture 1, Mixture 2 treatment has a higher removal efficiency in the mesophilic column than in the thermophilic column. Ethanol removal in the mesophilic column has increased by around

25-35%. Acetaldehyde removal efficiency has dropped between Mixture 1 and Mixture 2. The graphs for Mixture 2 also show fewer outlier readings.

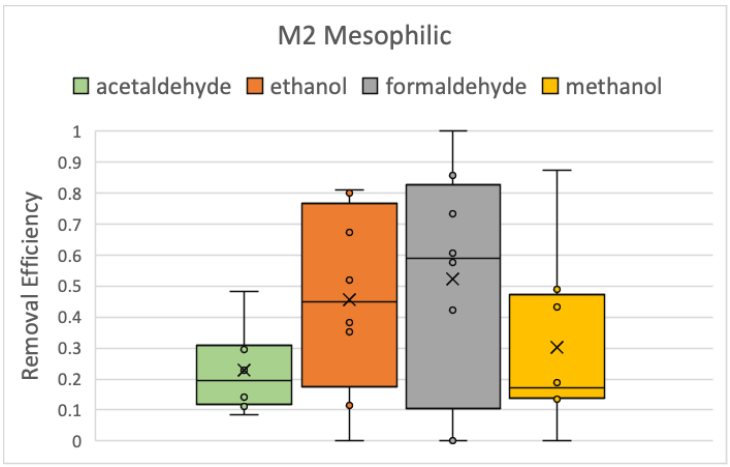



*Figure 4.5-Removal Efficiency of VOCs in Mixture 2 Under Mesophilic Conditions*

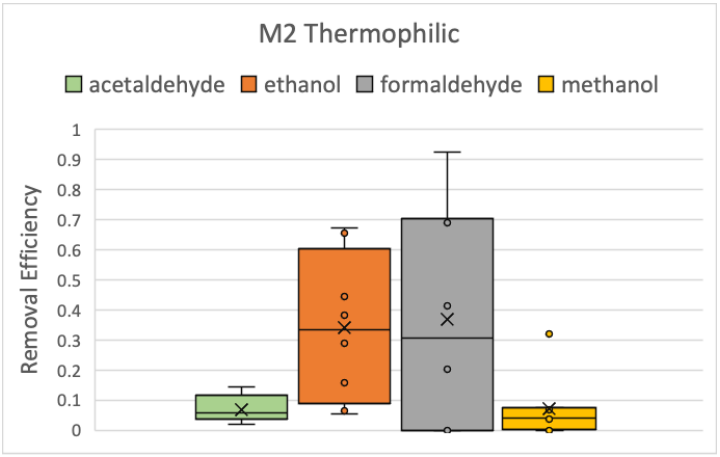



*Figure 4.6-Removal Efficiency of VOCs in Mixture 2 Under Thermophilic Conditions*

### 4.3.2 Influence of Bed Height on VOC Removal Efficiency

Measurements were taken at four different ports along both the mesophilic and thermophilic columns. These ports correlate to empty bed residence times (EBRT) of 0, 3.9, 12, and 31.3 seconds. Figures 4.7-4.10 show the average removal efficiency of the

individual compounds in both Mixture 1 and Mixture 2 in both mesophilic and thermophilic conditions.

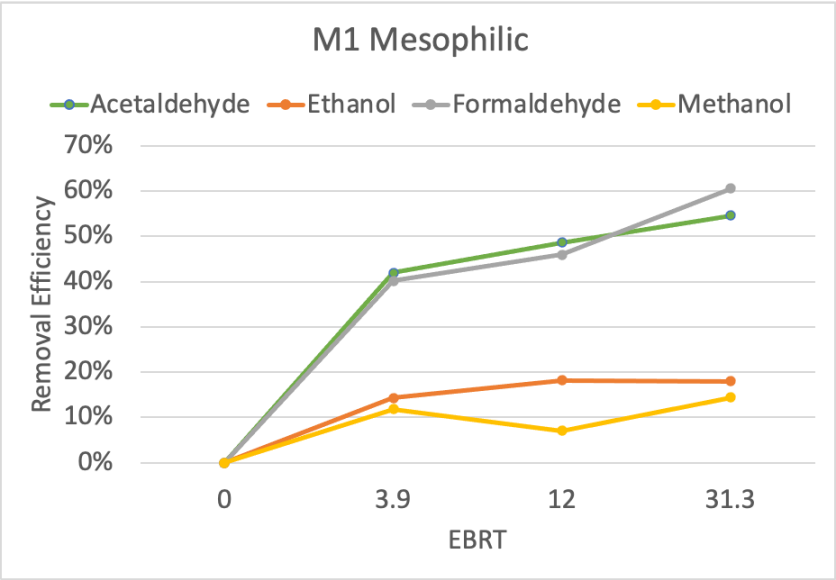



*Figure 4.7-Mixture 1 Removal Efficiency Based on Empty Bed Residence Time Under Mesophilic Conditions*

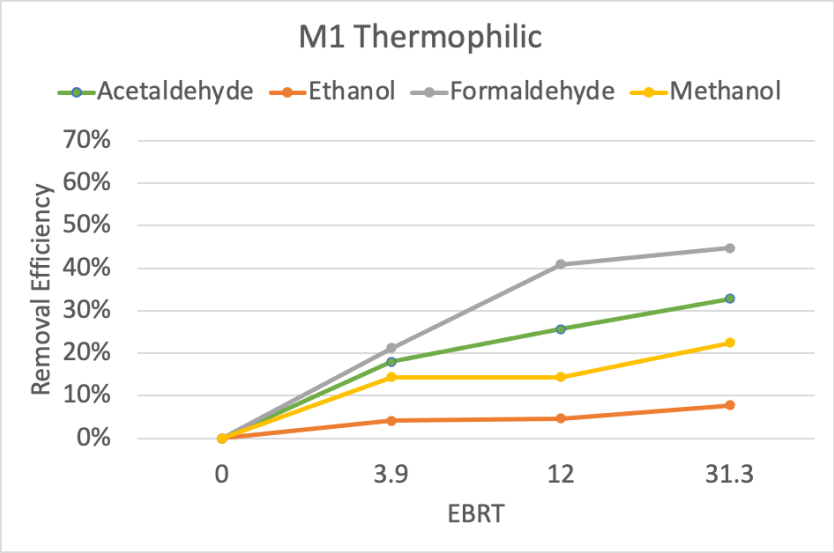



*Figure 4.8-Mixture 1 Removal Efficiency Based on Empty Bed Residence Time Under Thermophilic Conditions*

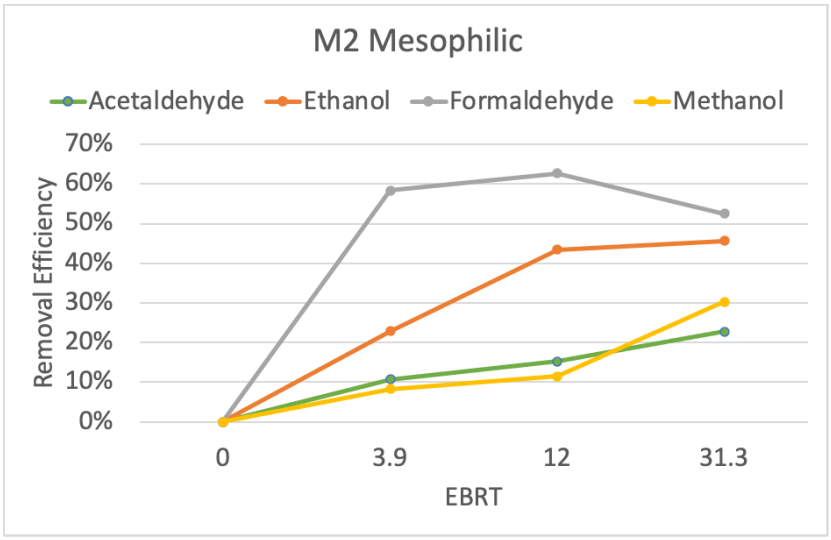



*Figure 4.9-Mixture 2 Removal Efficiency Based on Empty Bed Residence Time Under Mesophilic Conditions*

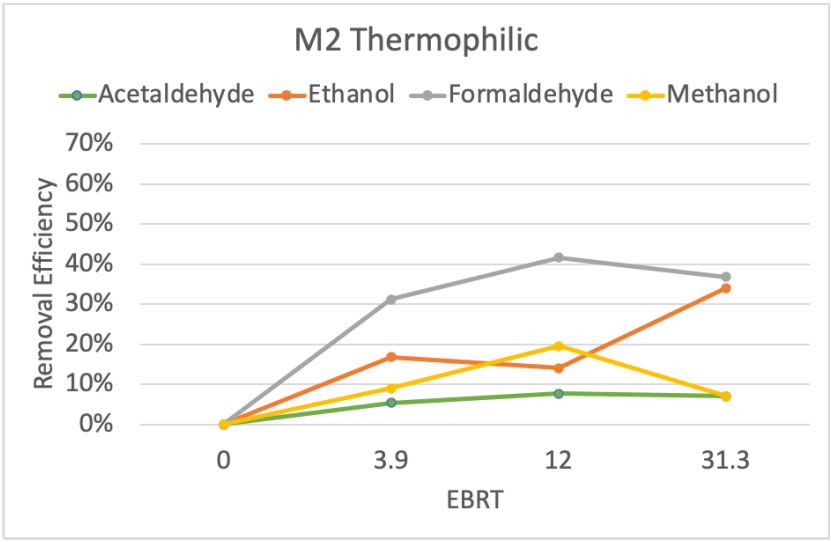



*Figure 4.10-Mixture 2 Removal Efficiency Based on Empty Bed Residence Time Under Thermophilic Condition*

The above graphs show that the removal efficiency for formaldehyde is always the highest out of the four compounds. They also show that treatment in the mesophilic column results in better removal efficiency than treatment in the thermophilic column. As the ethanol percentage in the mixture increases the removal efficiency of acetaldehyde

decreases. However, removal efficiencies are similar for ethanol even with the 50% increase in influent ethanol. This finding means that more ethanol is being treated as the influent amount of ethanol increases. From these graphs it is also apparent that the microbes in the columns have an affinity (either to adsorb or biodegrade) for formaldehyde, ethanol, acetaldehyde, and then methanol, in that order.

### 4.3.3 Performance of BTF Columns Based on Effluent

By looking at the effluent from the BTF columns, the environment inside the columns and how it can affect VOC treatment can be better understood. Each of the effluent aqueous results are an average of the two mixtures. This was done since the aqueous results were usually similar between the two concentrations of ethanol but different between the mesophilic and thermophilic columns. Figure 4.11 shows the average total suspended solids (TSS) in each column. This graph shows that there is a higher amount of TSS in the mesophilic column than in the thermophilic column. The average levels of chemical oxygen demand (COD) in each column are shown in Figure 4.12. The amount of COD ranges between 0.5-3.0 mg/L. The amount of COD in the effluent from the thermophilic column is higher than the COD amount in the mesophilic column effluent.

The influent into the columns and the effluent from each column was measured for pH level. Figure 4.13 shows the average pH in the influent nutrient solution (7.9). Figure 4.14 graphs the pH measurements over time in both the mesophilic and thermophilic columns. The pH in the mesophilic columns stays pretty constant at around 8.3. However, the pH of the thermophilic column decreases over time. This decrease was more pronounced after Mixture 2 was introduced to the column.

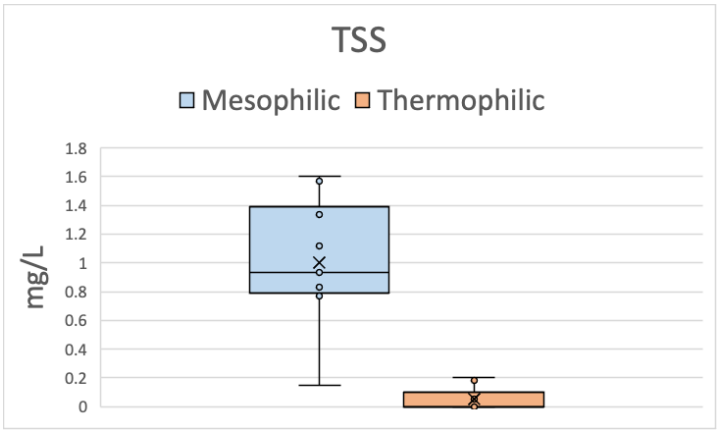



*Figure 4.11-Average Total Suspended Solids in Both the Mesophilic and Thermophilic Columns*

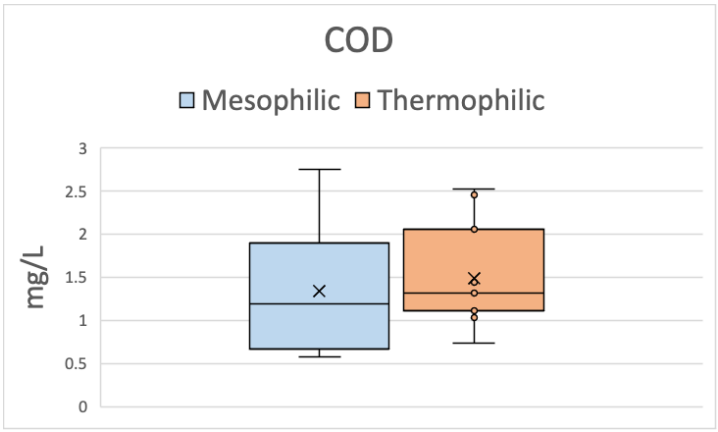



*Figure 4.12-Average Chemical Oxygen Demand (COD) in Both the Mesophilic and Thermophilic Columns*

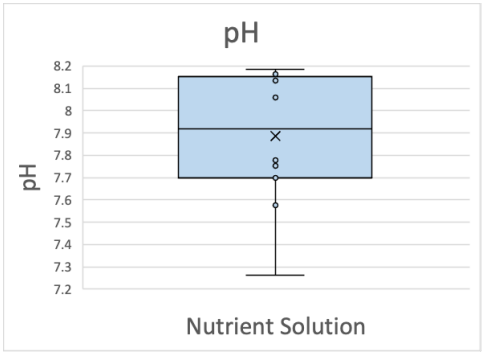



*Figure 4.13-Average pH in the Influent Nutrient Solution*

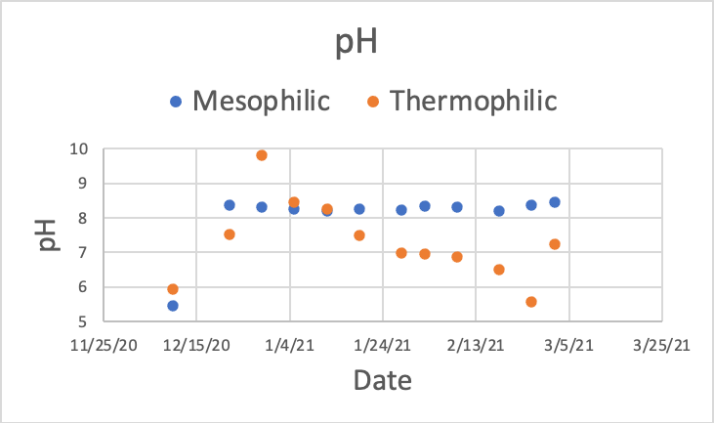



*Figure 4.14-pH Measurement Over Time in Both the Mesophilic and Thermophilic Columns*

## 4.4 Discussion

The results from the above section can help explain the effect of temperature and ethanol concentration on the BTF columns. The first observation was that it takes about two weeks for the columns to equalize to a new ethanol concentration and reach peak removal efficiency. A study by (Chen et al., 2010) agrees with this two-week period. However, the columns are very robust and can handle changes in VOC concentrations and nutrient solution amounts.

This study found that though treatment levels are similar, the mesophilic column has a higher average removal efficiency than the thermophilic column. There are a couple of reasons that this is the case. The first is due to the affect that temperature has on solubility of the VOCs. Duerschner (2019) determined that temperature can affect the solubility and thus treatment of VOCs. An increase in temperature results in a decrease in solubility. Due to the fact that treatment in a BTF is due to the interface between the VOCs and the biofilm on the column media, solubility is essential to treatment.

A second property that affects treatment is pH. A study by (Chen et al., 2010) demonstrated that a lower pH equates to a lower removal rate. Although bacteria grows at pH values ranging from 5 to 9, the preferred pH for bacterial activity is between 7 and 8 (Bak et al., 2017). The stability of this parameter is important as fluctuations of the pH more than 2–3 units is detrimental for microbial performance (Mudliar et al., 2010). Figures 4.12 and 4.13 give the pH results from this study. The influent nutrient solution and the effluent from the mesophilic column are similar and in the 8-9 pH range. The pH for the effluent of the thermophilic column however is decreasing from 8 to 5 as time goes by. This decrease in pH can in part be contributed to the byproducts of biodegradation of the compounds in the mixtures. The final products include acetate and formic acid. Thus, as the amount of compounds increase in the mixture the amount of acid produced will also increase.

Therefore, the lower removal efficiencies in the thermophilic column could be affected by both the reduced solubility of the VOCs due to temperature and the dropping pH values. A decrease in solubility means less carbon for the bacteria in the columns to consume (lower BOD) and the lower pH results in a less than ideal environment for microbial growth. These two circumstances result in less biomass growth (Environmental Business Specialists, 2011). This lack of biomass growth can be seen in the average total suspended solids (TSS) measurements for the two columns. Total suspended solids from the columns are made up of dead microbial matter. The creation of more biomass results in more solids being sluffed off into the effluent. The TSS is higher in the mesophilic column effluent than the thermophilic column effluent due to a larger amount of biomass in the former.

Lower removal efficiencies in the thermophilic column also result in the higher COD readings in the thermophilic column effluent. As the VOCs pass through the columns, what is not treated can end up in the aqueous liquid stream. These VOCs show up in the COD reading of the effluent.

The 100% increase in ethanol concentration in Mixture 2 also had effects on the treatment of the HAPs mixture. It is apparent that as the concentration of ethanol increases, the treatment of acetaldehyde decreases. This could be due to the microbes' having an affinity to certain compounds or the ethanol could be impacting the microbial consortium in a way that inhibits the degradation of acetaldehyde. More studies are needed to understand the interactions between the treatment of acetaldehyde and ethanol. Ethanol removal increased by around 25-35% between the two mixtures. This is due to the higher ethanol concentration in the second mixture. The increased ethanol concentration in the influent gas and the increase in ethanol removal could be changing the microbial culture to have a greater affinity to ethanol (thus impacting acetaldehyde treatment). A higher concentration could also mean that there is an increase in internal mass transfer of ethanol, thus resulting in an increase in treatment. The higher readings could also be due in part to the fact that higher concentrations of ethanol are read with more precision than lower concentrations by the GCMS.

The fact that formaldehyde has a higher removal efficiency than the acetaldehyde in all cases could be due to the fact that it has a shorter carbon chain than acetaldehyde and is thus more soluble. From looking at the figures above, the bacteria have an affinity (either to adsorb or biodegrade) for the VOCs in the following order: formaldehyde, ethanol, acetaldehyde, and then methanol.

## 4.5 Summary and Conclusions

Since 14.5 billion gallons of ethanol were consumed in the US in 2019 and this ethanol was produced primarily (82%) through dry-mill corn ethanol plants, it is important to find environmentally friendly ways of treating ethanol plant exhaust. Ethanol plants produce VOCs during production, and some of these VOCs are on the EPA's HAPs list. The industry standards for treating these VOCs use either a significant amount of water or energy (natural gas) to operate. This study looks at the treatment of a synthetic ethanol plant stream using an innovative industrial HAPs treatment method called a BTF. The BTF is made up of columns, a gas delivery system, a nutrient delivery system, and a sampling set-up. The mesophilic column had a higher removal efficiency than the thermophilic column. This could be due to solubility and pH. The higher temperature in the thermophilic column would negatively affect the solubility of the mixture. Past research has found that a lower pH also equates to a lower removal rate. When the compounds in the mixtures go through biodegradation the byproducts are acids which influence the pH in the columns. The influent nutrient solution and the effluent from the mesophilic column are similar and in the 8-9 pH range, however the thermophilic effluent pH decreased from 8 to 5 over time, therefore, resulting in not ideal pH levels in the thermophilic column.

The 100% increase in ethanol concentration in Mixture 2 also had effects on the treatment of the HAPs mixture. It is apparent that as the concentration of ethanol increases, the treatment of acetaldehyde decreases. Microbial affinity and/or ethanol impacting the microbial consortium may be the reason for this. Ethanol removal also increased by around 25-35% between the two mixtures due to the higher ethanol

concentration in the second mixture. This increase may be due to the microbial culture increasing its affinity to ethanol and/or an increase in internal mass transfer of ethanol. The higher readings could also just be due to the fact that the GCMS reads higher concentrations with higher accuracy. It was also found that the microbes had an affinity (either to adsorb or biodegrade) for VOCs in this order: formaldehyde, ethanol, acetaldehyde, and then methanol.

# CHAPER 5: ANALYSIS OF LIQUID STREAMS IN ETHANOL PLANTS

## 5.1 Introduction

An ethanol plant is composed of multiple processes and procedures that help distill ethanol from organic matter. These different processes result in different streams within the plant. In the plant diagram in Figure 3.1, 24 streams are labelled. These system-related streams are either aqueous or gaseous. The aqueous streams come from condensers, liquid streams from after different stages in the ethanol plant, and water that is used to regulate temperature during different processes. The gaseous streams are created by the exhaust from different processes.

This chapter focuses on the analysis of multiple aqueous streams within two different Nebraska ethanol plants (Plant A and Plant B). Both plants are dry-mill corn ethanol plants. However, as mentioned in Chapter 3, Plant A has an extra distillation column, a dryer, and a thermal oxidizer. It is also a larger and more complicated plant. Plant B does not have a second distillation column, and they do not dry their solids. Rather, they are able to distribute the solids as feed to farms nearby.

There are three reasons that these streams were analyzed. The first reason was to look at the streams as a possible nutrient solution option for a bio-trickling filter (BTF). The second reason was to look at where additional treatment would be needed to meet the Food and Drug Administration's (FDA) regulations on impurities in hand sanitizer. The last reason the liquid streams were analyzed was to understand the general composition

of different streams within the ethanol plant in case of intentional or unintentional discharge.

The analyzed streams were tested for: chemical oxygen demand (COD), total nitrogen (TN), total phosphorous (TP), pH, total suspended solids (TSS), and select volatile organic compounds (VOCs). These tests and their methods are listed and explained in detail in Chapter 3. Sample collection methods are also listed in Chapter 3.

### 5.1.1 Use of Ethanol Streams as Possible BTF Nutrient Streams

One of the essential parts of a BTF is the trickling fluid or nutrient solution. The trickling fluid keeps the BTF moist, pH constant, and provides the necessary nutrients for the microorganisms. The study by Smith et al. (1998) found that a nutrient solution that contained ratios of carbon/nitrogen (COD/N) =50 and nitrogen/phosphorous (N/P) =4 (wt./wt.) or a COD:N:P of 200:4:1 worked best. This conclusion was based on the BTF's performance and biomass produced. Most nutrient solutions, as mentioned in Chapter 2, have a pH between 7 and 8 (Smith et al., 1998; Sorial et al., 1995; Zehraoui et al., 2012).

The nutrient solution must also contain no more than a limited concentration of hydrocarbons, ethanol, and toxins that would limit microbial growth. If biological oxygen demand (BOD) test results are much lower that COD values (e.g., 10-20%) than there would be concern about toxicity. These results would mean that the bacteria in the BOD tests are being impacted by toxins in the stream while the chemicals in the COD are not being affected and are thus giving a correct reading. Treated waste streams may also cause problems in the BTF due to chlorine concentrations.

Ethanol concentrations can also be toxic in amounts around 40% by volume. The Toxicity is affected by the amount of ethanol in the mixture and the amount of time it is

in contact with the bacteria (Sissons et al., 1996). A study by Man et al. (2017) found that a solution with as low as 1.56% and usually around 6.25% by volume of ethanol can be inhibitory to some bacteria. In high molar concentrations, ethanol effects the aqueous environment and the central hydrophobic core of the plasma membrane of the bacteria cells. High concentrations of ethanol decrease the energy barrier and increase the permeability of the membrane to polar and charged molecules (Ingram, 1989). Since these waste streams are coming from different parts of an ethanol plant, there could be different amounts of ethanol in each stream.

Traditionally, BTFs are used for odor control at wastewater treatment plants (WWTPs). In these cases, effluent wastewater has been used as the nutrient solution. Although the wastewater is treated, it still contains a considerable level of nutrients. For lab-operated BTFs, a synthetic nutrient solution is usually created to include all the necessary nutrients, vitamins, and minerals.

At an ethanol plant, there are a few different options for a nutrient solution for a BTF. If there is a WWTP nearby, its effluent can be used as a nutrient solution. A synthetic stream could also be created such as the one used in this study. Nutrients would be added to well water at known ratios to create this synthetic nutrient stream. A third option would be to use a recycled ethanol plant stream, mixture of streams, or a stream/mixture of streams with additives as the BTF nutrient source.

In order to analyze the different samples, each one was tested for COD, TN, TP, pH, and TSS. The COD, TN, and TP measurements were each obtained using HACH TNT sampling kits. The testing procedure for each is listed in Sections 3.2.2-3.2.4.

Section 3.2.5 explains how pH readings of the samples were taken, and Section 3.2.5 explains the method used to find TSS in the samples.

### 5.1.2 Impurities in Hand Sanitizer

During the COVID-19 pandemic, the market for alcohol-based disinfectants increased dramatically. However, the FDA has strict limits on the impurity concentrations allowed in hand sanitizers. This changed on January 31, 2020 when the limits and associated regulations were raised to allow non-traditional manufacturers, such as ethanol plants, to help meet the demand (US HHS EPA CDER, 2021). According to the secretary of the US Department of Health and Human Services (HHS), these interim standards will be lifted once the public health emergency is over. Table 5.1 lists the interim and standard impurity limits. Once these interim standards are lifted, ethanol plants that want to continue producing hand sanitizer will need to lower their impurity levels. By understanding the make-up of different streams available in an ethanol plant, operators can better evaluate where they should be focusing their treatment to meet the standard limits.

*Table 5.5.1-Standard and Interim Impurity Limits for Alcohol-Based Hand Sanitizers.*

| **Impurity** | **Standard (ppm)** | **Interim (ppm)** |
|---|---|---|
| Methanol | 200 | 630 |
| Benzene | 2 | 2 |
| Acetaldehyde | *10 | 50 |
| Acetal (1,1-diethoxyethane) | *10 | 50 |
| Sum of all impurities | 300 | 300 |

*Acetaldehyde and acetal limits combined under standard impurity limits

This study looked at the amount of acetaldehyde, propanol, methanol, and acetal in each stream. These readings were determined by using the vacuum-assisted sorbent extraction (VASE) method in conjunction with a gas chromatography/mass spectrometry

(GC/MS). This method is able to analyze gaseous compounds within aqueous ethanol plant streams. This method is explained further in Sections 3.3.1. and 3.3.2.

## 5.2 Results and Discussion

This section focuses on the aqueous test results and GCMS analysis of the liquid ethanol plant streams. The aqueous test results will help determine if any of the ethanol plant streams or a combination of streams could be used as a BTF nutrient solution. The following GCMS analysis will give insight into the VOC impurities within each stream. The combined aqueous and gaseous sample data will provide a clearer picture of the actual composition of individual ethanol plant streams.

### 5.2.1 Nutrient Streams

Water tests were performed on streams from both Plant A and Plant B. Six samples for Plant A were analyzed and 17 from Plant B. A diagram of a common ethanol plant that lists locations and stream numbers for both plants can be found in Figure 3.1. A list of the streams tested from both Plants are listed in Table 5.2.

*Table 5.2-Plant A and Plant B Test Steams*

| Plant | Stream Numbers | Stream Names |
|---|---|---|
| B | 1 | Mix Tank Mash |
| B | 2 | Liquification Tank Mash |
| B | 3 | Fermentation Tank Beer |
| B | 4 | Beer Well Beer |
| B | 5 | Column Tops |
| B | 6 | Molecular Sieve Reject |
| B | 7 | Column Bottoms |
| B | 8 | Solids[d] |
| A, B | 9,10,11 | Thin Stillage (TS) |
| B | 12 | Corn Oil/Syrup |
| A, B | 13 | Evaporator Water (EV) |
| B | 15 | Well Water |
| A, B | 17 | $CO_2$ Scrubber Water ($CO_2$) |
| B | 18 | Recycled Cook Water (13 + 17) |
| A, B | 19 | Rectifier Column/ Reboiler Condensate (RC) |
| A, B | c | Cooling Tower Blow Down (CT) |
| A | c | Cooling Tower + Condenser water (CT + RC) (PC) |
| B | c | Process Condensate (EV+ RC+$CO_2$+ soft water) (PC) |

c- Streams with locations not listed in Figure 3.1
d-Aqueous tests were not performed on this stream

The comparison between each plants' streams in terms of water quality parameters of COD, TN, TP, pH, and TSS can be found in Table 5.3 below. These parameters will help define if any of these streams can be used as a nutrient solution in a BTF column. In order for any of these streams to be a possible nutrient solution, they need to have a pH value that is at least close to being between 7 and 8, a low amount of TSS (so not to clog up the columns), and the correct ratios of nutrients.

*Table 5.3-Aqueous Analysis Results/Water Quality Parameters*

| Plant | Stream | Sample Type | COD (g/L) | TN (g/L) | TP (g/L) | pH | TSS (g/L) |
|---|---|---|---|---|---|---|---|
| A | | Cooling Tower | 0.0435 ± 0.00065 | 0.0263 ± 0.00076 | 0.0116 ± 0.0001 | 7.35 ± 0.03 | <MDL |
| A | 17 | CO2 Scrubber Water | 48.7 ± 7.37 | 0.246 ± 0.00635 | <MDL | 5.25 ± 0.03 | <MDL |
| A | 13 | Evaporated Water | 5.59 ± 0.107 | 0.0113 ± 0.000163 | 0.00461 ±0.000199 | 3.16 ± 0.05 | 0.0117 ± 0.0153 |
| A | 19 | Rectifier Column | 0.0798 ± 0.00173 | 0.00151 ± 0.00033 | <MDL | 8.21 ± 0.55 | 0.00333 ± 0.0126 |
| A | 9,10,11 | Thin Stillage | 93.8 ± 2.72 | 3.917 ± 0.720 | 7.43 ± 0.0577 | 3.82 ± 0.04 | 19.6 ± 0.0577 |
| A | * | Process Condensate | 21.1 ± 0.202 | 0.31 ± 0.038 | 0.146 ± 0.00603 | 3.12 ± 0.06 | 0.757 ± 0.0416 |
| A | | Filtered Thin Stillage | 80.2 ± 9.16 | 2.43 ± 0.211 | 4.37 ± 0.0362 | 3.86 ± 0.062 | N/A |
| A | | Filtered Process Condensate | 17.8 ± 3.58 | 0.284 ± 0.0184 | 0.148 ± 0.0163 | 3.23 ± 0.065 | N/A |
| B | 1 | Mix Tank Mash | 305 ± 9 | 5.19 ± 0.25 | 3.85 ± 0.01 | 5.35 ± 0.04 | 108 ± 25 |
| B | 2 | Liquification Tank Mash | 285 ± 2 | 5.60 ± 0.68 | 2.97 ± 0.13 | 5.31 ± 0.01 | 98.6 ± 2.7 |
| B | 3 | Fermentation Tank Beer | 225 ± 7 | 7.27 ± 0.07 | 4.65 ± 0.14 | 4.68 ± 0.01 | 79.2 ± 6.0 |
| B | 4 | Beer Well Beer | 277 ± 2 | 6.27 ± 0.21 | 4.13 ± 0.2 | 4.08 ± 0.02 | 82.6 ± 10.8 |
| B | 5 | Column Tops | 1,150 ± 20 | 8.30 ± 0.98 | <MDL | 4.52 ± 0.04 | <MDL |
| B | 6 | Mole-Sieve Reject | 1,200 ± 0 | 7.35 ± 1.06 | <MDL | 3.78 ± 0.07 | <MDL |
| B | 7 | Column Bottoms | 122 ± 2 | 6.87 ± 1.01 | 4.58 ± 0.15 | 3.40 ± 0.02 | 90.2 ± 3.3 |

*-Not Labeled with a Number on the Figure, NM- Not Measured, N/A- Not Applicable, <DL- Under Detection Limit, DLs are as follows: COD = 1.0 mg/L, TN = 1.0 mg/L, TP = 0.5 mg/L, and TSS = 1.0 mg/L.

Table 5.3-Aqueous Analysis Results/Water Quality Parameters *(Continued)*

| Pl | Stream | Sample Type | COD (g/L) | TN (g/L) | TP (g/L) | pH | TSS (g/L) |
|---|---|---|---|---|---|---|---|
| B | 9,10,11 | Thin Stillage | 145 ± 2 | 7.13 ± 0.1 | 4.81 ± 0.07 | 3.36 ± 0.06 | 45.2 ± 5.5 |
| B | 12 | Corn Oil/Syrup | 51.5 ± 5.6 | 9.83 ± 0.01 | 8.41 ± 0.1 | 3.34 ± 0.01 | 89.4 ± 8.8 |
| B | 13 | Evaporated Water | 5.1 ± 0.1 | 0.0368 ± 0 | <MDL | 3.36 ± 0.05 | <MDL |
| B | 15 | Well Water | 0.014 ± 0 | 0.181 ± 0.028 | <MDL | 6.74 ± 0.12 | 0.0320 ± 0.0005 |
| B | 17 | CO2 Scrubber Water | 40 ± 1 | 0.201 ± 0.037 | <MDL | 5.78 ± 0.11 | <MDL |
| B | 18 | Recycled Cook Water | 17 ± 0 | 0.0385 ± 0 | <MDL | 5.06 ± 0.02 | 0.0266 ± 0.0011 |
| B | * | Reboiler Condensate | 2.4 ± 0.1 | 0.0037 ± 9e-4 | <MDL | 5.90 ± 0.02 | <MDL |
| B | * | Cooling Tower Blow Down | 1.3 ± 0 | 0.0012 ± 5e-4 | 0.0081 ± 0 | 8.32 ± 0.05 | 0.0557 ± 0.004 |
| B | * | Process Condensate (PC) | 0.03 ± 0 | 0.0269 ± 0.0019 | 0.0039 ± 0 | 7.69 ± 0.13 | 0.0326 ± 0.0023 |
| B | | Filtered Mix Tank Mash | 573 ± 30.3 | 3.73 ± 0.58 | 9.66 ± 0.23 | NM | N/A |
| B | | Filtered Liquification Tank Mash | 735 ± 106 | 4.03 ± 0.64 | 4.55 ± 0.27 | NM | N/A |
| B | | Filtered Fermentation Tank Beer | 225 ± 2.11 | 5.65 ± 0.31 | 4.54 ± 0.4 | NM | N/A |
| B | | Filtered Beer Well Beer | 298 ± 15 | 3.08 ± 0.37 | 4.08 ± 0.18 | NM | N/A |
| B | | Filtered Bottoms | 105 ± 4.96 | 5.38 ± 0.34 | 4.53 ± 0.13 | NM | N/A |
| B | | Filtered Thin Stillage | 89 ± 8.49 | 3.75 ± 0.44 | 4.37 ± 0.06 | NM | N/A |
| B | | Filtered Corn Oil/Syrup | 200 ± 26.8 | 6.25 ± 0.2 | 7.21 ± 0.16 | NM | N/A |

*-Not Labeled with a Number on the Figure, NM- Not Measured, N/A- Not Applicable, <DL- Under Detection Limit, DLs are as follows: COD = 1.0 mg/L, TN = 1.0 mg/L, TP = 0.5 mg/L, and TSS = 1.0 mg/L.

The aqueous sample results show that streams within both Plant A and Plant B vary greatly in make-up depending on where they are located in the plant. Streams from processes at the beginning of the plant have higher COD and TSS values. Streams that are used for temperature control, are condensate, or are made up mostly of water that is added into a process all have low amounts of nutrients.

In order for a stream to be used as a nutrient solution, it cannot have any microbial inhibitors. This becomes apparent in the cooling tower water stream. Chlorine is added to this stream in order to prevent bacteria from growing in the temperature regulation system. This same chlorine would affect the growth of bacteria that is needed in the BTF if the cooling tower water stream was used as a nutrient solution. Hydrocarbons can also be toxic to microorganisms. Due to high ethanol content in some of the streams, these streams would not be a good choice for a nutrient stream. The streams that occur before ethanol is removed in the rectifier column will have higher ethanol concentration than streams after ethanol removal, and thus are not good choices for BTF nutrient streams.

Biological oxygen demand (BOD) tests were completed on samples from Plant A. These tests did not produce valid results due to either having a difference between initial and final dissolved oxygen (DO) of less than 2 mg/L or having a final DO value less than 2 mg/L. When these results are compared to their COD values, it seems likely that the wastewater streams contained microbial inhibitors. These inhibitors could be chlorine in the case of the cooling tower water or higher ethanol concentrations in the case one of the streams before ethanol extraction (streams 1-6).

External factors can also affect the wastewater streams being tested. For instance, bad fermentation batches can be due to an infection. This causes high levels of acetic acid to be formed in the fermenter, which could cause the stream to be toxic to the microbes in the BTF. The volume of stream flow available would also affect which stream could be selected as a potential nutrient stream. Additionally, the fermenters are shut down periodically in order to give them a thorough cleaning. This would affect the ability of some flows to be used continuously as needed for the microbes' growth in the BTF. To avoid this problem, either a tank would need to store the stream for use during shutdowns or only streams that were not affected by the fermenter shut down could be considered.

However, if a storage tank is used there is a chance that the chemistry of the stream may change. Therefore, if a stream looks viable but needs to be stored in a tank for a period of time, tests should be done to determine the effects on the stream's nutrient composition.

Once a stream has been determined to be free of microbe inhibitors, contain appropriate nutrients, and be readily available at all times, a further analysis of the nutrient make-up of the stream can provide insight into whether or not an ethanol plant stream is a good candidate for a BTF nutrient solution. In order to evaluate the effectiveness of the streams as possible BTF nutrient solution options, the values from Table 5.3 are redefined as C:N:P ratios in Table 5.4. A BTF nutrient solution should have a C:N:P ratio of around 200:4:1. The ratios in the table are listed based on phosphorus being 1 part or, if there is no phosphorus in the stream, with the nitrogen as 4 parts. This method makes it easier to compare ratios between streams. As seen in the Table, none of the streams that were tested meet this ratio perfectly. It should also be noted that the

carbon that is listed is based solely on the aqueous COD measurements. In reality, the VOCs that are in the stream that is being treated will contribute to the total carbon amounts. Thus, due to the high VOC content of the ethanol plant streams that will be treated by the BTF, a lower C value than 200 should be considered when selecting streams as possible BTF nutrient solution options.

*Table 5.4-Stream C : N : P Ratios*

| Plant | Stream | Carbon | Nitrogen | Phosphorus |
|---|---|---|---|---|
| A | Cooling Tower | 3.7 | 2.3 | 1 |
| B | Cooling Tower | 160 | 0.15 | 1 |
| A | $CO_2$ Scrubber Water | 792 | 4 | 0 |
| B | $CO_2$ Scrubber Water | 796 | 4 | 0 |
| A | Evaporated Water | 1,210 | 2.4 | 1 |
| B | Evaporated Water | 556 | 4 | 0 |
| A | Rectifier Column | 211 | 4 | 0 |
| B | Reboiler Condensate | 2,600 | 4 | 0 |
| A | Thin Stillage | 12.6 | 0.53 | 1 |
| B | Thin Stillage | 30 | 0.9 | 1 |
| A | Process Condensate | 145 | 2.12 | 1 |
| B | Process Condensate | 7.7 | 6.9 | 1 |
| A | Filtered TS | 18.4 | 0.56 | 1 |
| B | Filtered TS | 20.4 | 0.86 | 1 |
| A | Filtered PC | 120 | 1.91 | 1 |
| B | Mix Tank Mash | 79 | 1.3 | 1 |
| B | Liquification Tank Mash | 96 | 1.9 | 1 |
| B | Fermentation Tank Beer | 48 | 1.6 | 1 |
| B | Beer Well Beer | 67 | 1.5 | 1 |
| B | Column Tops | 556 | 4 | 0 |
| B | Mole-Sieve Reject | 652 | 4 | 0 |
| B | Column Bottoms | 27 | 1.5 | 1 |
| B | Corn Oil/Syrup | 6.3 | 1.2 | 1 |
| B | Well Water | 0.308 | 4 | 0 |
| B | Recycled Cook Water | 1,770 | 4 | 0 |
| B | Filtered Mix Tank Mash | 59.3 | 0.39 | 1 |
| B | Filtered Liquification Tank Mash | 162 | 0.89 | 1 |
| B | Filtered Fermentation Tank Beer | 44.4 | 0.56 | 1 |
| B | Filtered Beer Well Beer | 73.1 | 0.75 | 1 |
| B | Filtered Column Bottoms | 23.1 | 1.19 | 1 |
| B | Filtered Corn Oil/Syrup | 31.5 | 0.91 | 1 |

Referring to the Table above, none of the mixtures have a 4:1 N:P ratio. The evaporator water from Plant A has a ratio of 2.4:1 which means it contains just over half the amount of nitrogen needed and the process condensate from plant B has a ratio of 6.9:1 which is close but contains too much nitrogen.

Looking at C:P ratios, there are no perfect 200:1 ratios. However, filtered liquification tank mash from Plant B has a ratio of 162:1, cooling tower from Plant B has a ratio of 160:1, and the process condensate from Plant A has a ratio of 145:1. None of these have the correct N:P ratio (N is too low) though.

Furthermore, if we look at C:N ratios (looking for >200:4) the rectifier column water from Plant A is the closest at 211:4 but the stream contains no phosphorus.

Acknowledging the fact that none of the streams are a perfect nutrient stream for a BTF, another possible option would be to mix multiple waste streams. However, when any of the streams are mixed the resulting mixture will either never contain enough nitrogen, contain too much phosphorus, contain too much carbon, or the total nutrients in the solution per liter would be too low to work as a nutrient solution.

The final option would be to use a stream as a base nutrient stream and add additives in order to create the desired ratio. The best candidate stream for this option would be the rectifier column (RC) from Plant A. This stream would reach the desired ratio by just adding phosphorus. Other options would be to add nitrogen to the filtered liquification tank mash from Plant B, cooling tower from Plant B, or the process condensate from Plant A.

Ethanol plant streams are dependent on plant operation however, and thus will not always be the exact same composition each time. In order to counteract this, if a waste

stream with additives is used, continual analysis of the waste stream will need to be completed in order to know how much of the additive is needed at a given time to keep the ratios optimal. Therefore, it may be more efficient to just create a mixture using fresh water and adding nutrients. This option, though not as easy as just using a stream from the plant, will guarantee that the ratio of nutrients will always be the same and will be exactly what the BTF column needs.

The final option of using effluent from a WWTP becomes the best option when lack of proximity isn't an issue. If the effluent can be transferred directly from the WWTP to the BTF with little to no human interference, then using it as a nutrient solution constitutes the least amount of work. It is also a form of reuse, may be free, and prevents the effluent from entering nearby water sources directly.

### 5.2.2 Analysis of Gaseous Impurities in Ethanol Plant Streams

In order to compare existing impurity levels to both the interim and normal impurity levels, GCMS analysis was completed on gaseous extraction from both the liquid and solid portions of the 17 streams from Plant B. There are three reasons why only streams from Plant B were analyzed: Plant A's management changed during the course of the study, the pandemic limited the ability to collect samples, and Plant B was the plant that was focused on creating ethanol for hand sanitizer that meets the FDA's regulations on impurities, not plant A. Concentrations of the compounds acetaldehyde, propanol, methanol and acetal were measured. Results from the GCMS tests are shown in Table 5.5.

*Table 5.5-Plant B Process Streams' COD and Impurity Concentrations*

| **Process Streams** | | **Liquid Portion** | | | | | **Solid Portion** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| # | Name | COD (g/L) | Acetaldehyde (mg/L) | Propanol (mg/L) | Methanol (mg/L) | Acetal (mg/L) | Acetaldehyde (mg/L) | Methanol (mg/L) | Propanol (mg/L) | Acetal (mg/L) |
| 1 | Mix Tank Mash | 310 | <DL | <DL | <DL | <DL | 11 | <DL | 3.6 | <DL |
| 2 | Liquefaction Tank Mash | 290 | <DL | <DL | <DL | <DL | 360 | 33 | <DL | <DL |
| 3 | Fermentation Tank Beer | 230 | 130 | 14 | 390 | <DL | 220 | 860 | <DL | 2 |
| 4 | Beer Well | 280 | 260 | 12 | 170 | <DL | 160 | 990 | 5 | 2 |
| 5 | Column Tops | 1,200 | 610 | 130 | 380 | 130 | NS | NS | NS | NS |
| 6 | Mole Sieve Reject | 1,200 | 580 | 13 | 1700 | 10 | NS | NS | NS | NS |
| 7 | Column Bottoms | 120 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 3 |
| 9, 10, 11 | Thin Stillage | 150 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.3 |
| 12 | Corn Oil/Syrup | 52 | <DL | 10 | <DL | <DL | <DL | <DL | <DL | 2.7 |
| 13 | Evaporated Water | 5 | <DL | <DL | <DL | <DL | NS | NS | NS | NS |
| 15 | Well Water | 14 | <DL | <DL | <DL | <DL | NS | NS | NS | NS |
| 17 | $CO_2$ Scrubber Water | 40 | <DL | <DL | 77 | <DL | NS | NS | NS | NS |
| 18 | Recycled Cook Water | 17 | <DL | <DL | <DL | <DL | NS | NS | NS | NS |
| * | Cooling Tower Blow Down | 1 | <DL | <DL | <DL | <DL | NS | NS | NS | NS |
| * | Cooling Tower Blow Down + RO Reject | <DL | <DL | <DL | <DL | <DL | NS | NS | NS | NS |

NS = no solids in the process stream and <DL = under detection limit. DL is as follows: COD = 1.0 mg/l; acetaldehyde = 7.5 mg/l; propanol = 9 mg/l; methanol = 9 mg/l; and acetal = 5 mg/l.

Figures 11 and 12 in Appendix D present the flow throughout the plant in terms of the impurity concentration and flow rate of the liquid samples and impurity concentrations in terms of COD as well as the overall COD concentration for the liquid samples. High concentrations of impurities were found in the following streams: beer 3, beer 4, column tops 5, and mole sieve reject 6. The relation between column tops 5 and mole sieve reject 6 is important because any mass lost between the two streams is found in the final ethanol product.

### *Acetaldehyde and Acetal*

Acetaldehyde and acetal are two of the impurities regulated in hand sanitizers by the FDA. The allowable interim combined concentration of the two compounds in the final ethanol product is 50 mg/L. Acetaldehyde appears in mash 1, mash 2, beer 3, beer 4, column tops 5, and mole sieve reject 6 — the concentrations of which are larger than the impurity limit for all samples, except mash 1. There is an acetaldehyde mass-flow difference of 80 g/min between column tops 5 and mole sieve reject 6. This 80-g/min difference is evident in the final product (Stream 25). Further treatment of either column tops 5 or final product 25 is necessary to reduce acetaldehyde to below FDA limits.

The concentration of acetal is first detected in the solid portion of beer 3 and beer 4 streams. After distillation, some of the acetal remains in the solid portions of bottoms 7, thin stillage 9/10/11, and corn oil/syrup 12 streams but at concentrations below 3 mg/L. The acetal concentration of column tops 5 is well above the FDA limit at 130 mg/L. There is a mass difference of 21.5 g/min acetal between column tops 5 and mole sieve reject 6, which will show up in final product 25. Thus, both acetaldehyde and acetal

concentrations must be reduced in either column tops 5 or final product 25 to meet the impurity limits set by the FDA.

### *Methanol, Propanol, and COD*

Methanol is one of the impurities regulated by the FDA for hand sanitizers. The FDA limit for methanol is 630 mg/L under interim conditions and 200 mg/L under normal standards. Methanol concentrations are over the normal FDA limit in beer 3, column tops 5, and mole sieve reject 6. An interesting occurrence is the accumulation of methanol between the distillation column and the molecular sieve owing to the properties of methanol. Since methanol is extremely volatile and has a lower boiling point than ethanol, the majority of the methanol should be found at the top of the distillation column (column tops 5). Methanol also has a small molecule size, which is comparable to water, and thus the molecular sieve can filter and send it back to the column. As methanol is filtered out by the molecular sieve, the concentrations of methanol in final product 25 should be below the specified FDA limits.

Propanol is not one of the regulated impurities in hand sanitizer. Propanol concentrations are low throughout the plant streams except column tops 5, wherein the concentration is 130 mg/l. COD concentrations are approximately 300 mg/L for the first four process streams. The spike in column tops 5 and mole sieve reject 6 streams are owed to the high concentration of ethanol being released from the distillation-column top. COD concentrations dropped in subsequent streams coming out of the distillation-column bottom.

### 5.2.3 Composition of Waste Flows

The results from this study help to describe the make-up of ethanol plant streams. This is important information for multiple reasons. In the unfortunate event of a leak within a plant, understanding the general make-up of the stream can help with cleanup and determining the environmental impact of the spill. Another case in which this information could be useful is in helping plants reduce their greenhouse gas (GHG) footprint and increase their market share and profitability. An example of this is California's low-carbon fuel standard (LCFS) carbon credit system which incentivizes creating low-carbon intensity fuels (California Air Resources Board, 2021). By understanding streams, plants can work to lower their GHG footprint by targeting different processes in the plant for further treatment. The final reason for wanting to understand the makeup of ethanol plant streams is to be able to create an ideal product. By understanding where different impurities are coming from during the process of creating ethanol, more targeted treatment can be applied.

## 5.3 Conclusions

This chapter analyzed the streams of two different ethanol plants for three reasons. The first was to see if any of the streams had the nutrient makeup that could be used as a nutrient solution in a BTF. It was determined that neither of the two plants had a stream the met the exact C:N:P ratio of 200:4:1. After consideration of different mixtures of streams it was determined that a mixture of different streams would also not meet the required ratio. Thus, in order to make a nutrient stream for a BTF at an ethanol plant, the three remaining options are WWTP effluent, a waste stream with nutrients added, or well

water with nutrients added. The choice between these options would be made based on cost, location, and time and would be plant specific.

Ethanol plants transitioning into the production of alcohol-based disinfectants must meet impurity limits as set by the FDA. For Plant B, the column tops 5 or the final product 25 processes streams will need to be further treated to meet impurity limits as set by the FDA. The acetaldehyde and acetal concentrations in column tops 5 are well over the limits set by the FDA and the concentration of methanol in column tops 5 is below the interim impurity limits but will need to need be lowered further to meet limits under normal conditions.

The results from these tests give a clearer picture of the composition of different streams within ethanol plants. This information can be used by ethanol plants, regulators, and fellow researchers to help build better, safer, and cleaner ethanol plants.

# CHAPER 6: CONCLUSIONS

## 6.1 Summary of Findings

In the United States, there are 202 ethanol plants, and 82% of ethanol is produced through the fermentation of corn at dry-mill ethanol plants (BBI International, 2021). Volatile organic compounds (VOCs), some of which are on the US Environmental Protection Agency's (EPA) hazardous air pollutants (HAPs) list, are created and released during the fermentation process and the drying of dryer distiller grains with solubles (DDGS). A bio-trickling filter (BTF) is an innovative alternative to traditional air pollution control methods that uses less water and no natural gas.

In this study, HAPs mixtures with two different concentrations of ethanol — mixtures similar in composition to ethanol plant exhaust — were tested in a lab-scale BTF, and the composition of each mixture is listed in Table 4.1. The mixtures were tested in both a mesophilic (21ºC) and a thermophilic (60 ºC) column. The mesophilic column had a higher removal efficiency than the thermophilic column. This could be due to greater solubility of the compounds at 21ºC and a more stable pH environment. The higher temperature in the thermophilic column negatively affects the solubility of the mixture. Past research has found that a lower pH also equates to a lower HAPs removal rate which this study supports. The influent nutrient solution and the effluent from the mesophilic column are similar and in the 8-9 pH range, however, the thermophilic effluent pH decreased from 8 to 5 over time. This decrease results in non-ideal pH levels for microbes in the thermophilic column.

The 100% increase in ethanol concentration in Mixture 2 also had effects on the treatment of the HAPs mixture. It is apparent that as the concentration of ethanol increases, the treatment of acetaldehyde decreases. Microbial affinity and/or ethanol impacting the microbial consortium may be the reason for this. Ethanol removal also increased by around 25-35% between the two mixtures due to the higher ethanol concentration in the second mixture. This increase may be due to the microbial culture increasing its affinity to ethanol and/or an increase in internal mass transfer of ethanol. The higher readings could also just be due to the fact that the GCMS reads higher concentrations with higher accuracy. It was also found that the microbes had an affinity (either to adsorb or biodegrade) for VOCs in this order: formaldehyde, ethanol, acetaldehyde, and then methanol.

This thesis also looked at an analysis of aqueous ethanol plant streams from two different ethanol plants. It was determined that neither of the two plants had a stream that met the exact C:N:P ratio of 200:4:1 necessary for use as a nutrient solution in a BTF. After consideration of different mixtures of streams, it was determined that a mixture of different streams would also not meet the required ratio. Thus, in order to make a nutrient stream for a BTF at an ethanol plant, the three remaining options are WWTP effluent, a waste stream with nutrients added, or well water with nutrients added. The choice between these options would be based on cost, location, and time and would be plant specific.

The final study looked at ethanol plants transitioning into the production of alcohol-based disinfectants and what they must do to meet impurity limits as set by the FDA. For Plant B, the column tops 5 or the final product 25 processes streams will need

to be further treated to meet impurity limits as set by the FDA. The acetaldehyde and acetal concentrations in column tops 5 are well over the limits set by the FDA and the concentration of methanol in column tops 5 is below the interim impurity limits but will need to need be lowered further to meet limits under normal conditions.

## 6.2 Recommendations for Future Work

Here are some recommendations for future work involving BTF testing as it relates to treating VOCs from ethanol plant exhaust. One of the conclusions of Chapter 4 was that as ethanol concentration increased the removal efficiency of acetaldehyde decreased. It is recommended that a future study examine the relationship between the treatment of ethanol and acetaldehyde — since both make up a significant portion of ethanol plant exhaust — to verify the findings of this study.

Further tests should be run on the treatment of HAPs mixtures with higher ethanol concentrations in BTFs. This study looked at mixtures with ethanol concentrations that are on the low end of what could be expected in an ethanol plant exhaust stream. In order to get a full understanding on the effect of ethanol concentration on BTFs, more tests with concentrations of ethanol up to 5,000 ppm should be completed.

This study and other related literature have found that pH plays a role in the treatment of VOCs in BTFs. Future tests should work to keep the pH of the columns between 7-8. By placing a pH probe in the columns, the pH can be monitored in real time. This data would be used to adjust the pH of the nutrient solution going in. By using more buffer solution and/or adding HCl or NaOH to the nutrient solution, the pH can be kept constant. This is especially important for the thermophilic column where this study saw a large decrease in pH over time.

During the BTF testing, nitrate and $CO_2$ tests were attempted, but the results were not conclusive. Thus, when completing nitrate tests in the future, all attempts should be made to complete the tests immediately after sampling. The results of these tests will help further the understanding of both treatment and biological activity in the columns.

This study also brings up the need to understand what microbes are currently in the columns and how they are affected and change depending on mixture composition, pH, and temperature. Tests of the bacteria at multiple levels in the column would be important to help understand how to foster the best bacteria for ethanol plant exhaust stream treatment.

Another potential study that could be completed, would be to look at the use of anaerobic BTFs. In an anaerobic process, short chain fatty acids are synthesized into medium chain fatty acids. One of the goals of such a study would be to consider if the products from this process could be converted into a valuable byproduct.

The ultimate goal would be to build a pilot BTF at an actual ethanol plant. The BTF would treat actual ethanol plant exhaust and the influent and effluent would be tested to prove the feasibility of a BTF treating actual ethanol plant exhaust.

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# APPENDIX A: OPERATIONAL PROCEDURES

## A1 Seeding of BTF Beds

(Duerschner, 2019)

The BTF beds were seeded using two different inoculants: anaerobic sludge and a slurry prepared from cooking compost. To seed using anaerobic sludge:

1. Estimate the void volume of the bed.
2. Collect the estimated volume of sludge. Then, dissolve two grams of glucose per liter in the sludge.
3. Close the liquid drain of the BTF column. Remove all gas sampling tubes and replace the annular septa on the sampling ports with the solid septa.
4. Pour the sludge over the BTF bed until all the media is submerged. Check the sludge level in the bed over the next few hours; it will decline as bubbles escape the bed. Add additional sludge as needed.
5. Leave the media submerged overnight.
6. Drain the sludge from the bed. Draining through the lowest gas-sampling port will prevent accumulation of solids on the permeable-media-support plate and minimize clogging.

To seed using a cooking compost slurry:

1. Estimate the void volume of the bed and collect that quantity of deionized water.
2. Compute half the volume of water collected and collect this amount of cooking compost.

3. Mix the cooking compost into the water and add two grams of glucose per liter of the final volume.
4. Pour the slurry through a mesh sieve to remove large debris and over the BTF bed until the media is submerged. Check the liquid level over the next few hours; it will decline as bubbles escape the media. Add additional slurry as needed.
5. Leave the media submerged overnight.
6. Drain the slurry from the bed. Draining through the lowest gas sampling port will prevent accumulation of solids on the permeable-media-support plate and will minimize clogging.

## A2 Preparation of the Water Trap

(Duerschner, 2019)

A water trap was used in the sample line following the multidirectional valve (to prevent excess moisture from entering the GCMS, MicroGC, and FTIR). The trap consisted of a 250 mL Erlenmeyer flask packed with anhydrous sodium sulfate and equipped with a rubber stopper with two ¼" holes. The sample gas enters a longer 1⁄4'' stainless steel tube to the bottom of the flask and exits through the shorter 1⁄4'' stainless steel tube near the top of the flask, trapping water droplets.

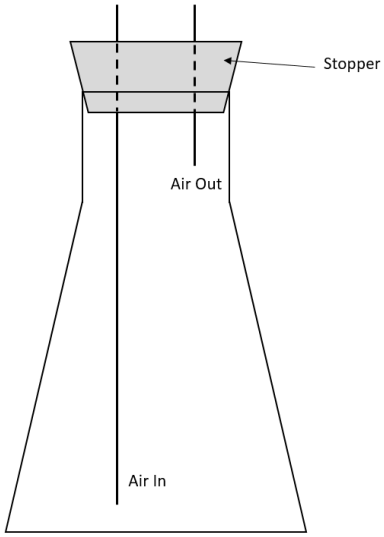



*Figure A.1-Schematic of water trap design used to keep moisture out of the GCMS, GC, and FTIR*

## A3 Preparation of Nutrient/Buffer Solution

(Duerschner, 2019)

Concentrated stock solutions were prepared containing all necessary nutrients for microorganism growth and stored in four-liter amber glass bottles. The composition of these stock solutions is shown in Table B1 in Appendix B. To prepare the nutrient solution, the stock solutions were diluted appropriately. The dilution factors for the stock, ferric chloride, spike, buffer, and vitamin solutions are respectively 2,257, 6,250, 100, 87.7, and 8,772. The nutrient solution was prepared in five-gallon batches, and each batch lasted for approximately one week.

## A4 Preparation of HAP and Ethanol Solutions

(Duerschner, 2019)

As mentioned in the Chapter 3, a syringe pump was used to control the infusion of a HAPs and ethanol solution into an air stream to create a desired concentration in the BTF Columns. This procedure describes the preparation of the solution used to fill the

syringes. The syringes could not be filled with pure compounds. Due to the low boiling point of acetaldehyde (one of the HAPs compounds), the low vapor pressure inside the syringes would expel the liquid at an uncontrolled rate. To combat this, a diluted solution of the mixture was used.

A four-liter batch size was created of each ethanol concentration at the beginning of each testing cycle. Care must be taken while preparing these solutions because the heat produced by mixing the compounds and water causes the compounds to boil at the mixing interface. Therefore, always mix compounds into water — never water into compounds —, and always prepare the solutions in a fume hood. Additionally, wear butyl rubber gloves with a minimum thickness of 7 mm when handling pure compounds such as acetaldehyde, as it is able to penetrate standard nitrile gloves.

The operating procedure for the preparation of Mixture 1 solution is:

1. Fill a four-liter volumetric flask with 3032 mL of deionized water. If time allows, refrigerate this water before preparing the solution. Doing so will minimize the amount of vapors produced during mixing when the compounds are added.
2. Measure 212 mL of ethanol, 356 mL of formalin, and 400 mL of acetaldehyde.
3. Slowly pour the ethanol, formalin, and acetaldehyde into the volumetric flask. Use a funnel to minimize spillage. Do not hold the outside of the funnel flush with the mouth of the volumetric flask, as this will trap vapors in the headspace of the flask. If the vapor pressure becomes great enough, the vapors can erupt dangerously through the liquid in the funnel.

4. Seal the jar with an airtight cap for storage, and refrigerate it until the solution is cool enough for general storage.
5. Run the mixture through the syringes at a rate of 19.960 ul/min for the correct flow rate of compounds into the columns.

A5 Aqueous Test Instructions (BTF Influent and Effluent)

The operating procedure for completing COD, TSS, VSS, and pH measurements on mesophilic and thermophilic effluents and pH measurements on influent nutrient solution is as follows:

1. Put six paper filters in the 100°C oven roughly 24 hours before the TSS test will be performed. Label the aluminum trays from 1-6 using a pen to scratch the number into the bottom of each tray (the ink will burn off).
2. When arriving at the lab on the day of tests, turn on the Hack company DR 2800 spectrophotometer, the reactor using the switch on the back, and the oven (set to 550°C).
3. Pour the contents of the effluent column samples into the two-liter beakers, and make sure they are labelled properly.
4. Gather a 50 mL volumetric flask and two small beakers. The two beakers will eventually contain the diluted samples and should be able to hold just over 50 mL (these will be referred to as beakers A and B).
5. Use the 1 mL pipet to transfer 2 mL of sample into the 50 mL volumetric flask (start with the mesophilic effluent).
6. Fill the rest of flask up to the 50 mL line with DI water.

7. Mix and move the diluted solution to beaker A.
8. Rinse out the 50 mL volumetric flask.
9. Repeat steps 5-7 with thermophilic effluent as the sample and beaker B as the diluted solution container.
10. Gather six Hach TNT 820 COD test vials and number them on the lid with a sharpie. Shake the vials until no sediment is at the bottom and place them in the red tray.

***Wait to do the next step until the thermometer on the reactor reads 150°C.***

11. Uncap the first COD vial and transfer 2 mL of the diluted sample in beaker A into the vial using the 1 mL pipet. Turn the vial over 2-3 times and place into the heating block.
12. Repeat with the remaining vials, remembering to switch to beaker B for vials 4-6.
13. Start a timer for 2 hours when the last vial has been placed on the heating block.
14. For the pH test, pour some sample from the mesophilic and thermophilic (non-diluted) beakers into their own small beakers. In a third small beaker, gather some nutrient solution. Make sure these beakers are labelled. Grab a fourth small beaker to use for runoff from cleaning the pH probe. You will also need a squeeze bottle of DI water, which is usually next to the probe, and Kimwipes.
15. Carry the four beakers, data sheet, and a box of Kimwipes into the teaching lab.
16. Turn on the pH probe with the power button in the center. Remove the probe from the storage solution, spray it with DI water (allowing the excess to run into the empty fourth beaker). Wipe down with a Kimwipe.

17. Place the probe in the mesophilic solution and press the measure button on the control panel. Wait until the reading normalizes and the “pH” icon on the side of the screen stops flashing. Record the pH reading and repeat two more times for a total of three readings. Spray down the probe with DI and wipe it off between each measurement
18. Repeat step 17 for the thermophilic effluent sample and the nutrient solution sample.
19. Once the oven has reached 550°C, transfer the filters into the oven. Be sure to use the orange gloves when handling things going into or out of this oven.
20. Set a timer for 30 minutes.
21. Remove the filters from the oven and immediately place them in the desiccator in the teaching lab. The less time these are out in the open the better, as they will absorb moisture from the air rapidly as they cool, affecting the results of the test.
22. It will take roughly 2 minutes for these to cool fully in the desiccator. Once they have cooled, take them out one by one and weigh them.
23. To weigh, take one tray out of the desiccator, grab the filter with tweezers, tare the scale with the aluminum tray on it, and then place the filter on it and record the weight once it stabilizes.
24. Repeat step 23 until all filters have been weighed.
25. The next step is to filter the sample through the papers. To prepare, turn on the vacuum pump, gather the two-liter beakers of solution, and set up the filtration system referencing Figure A.2 below.

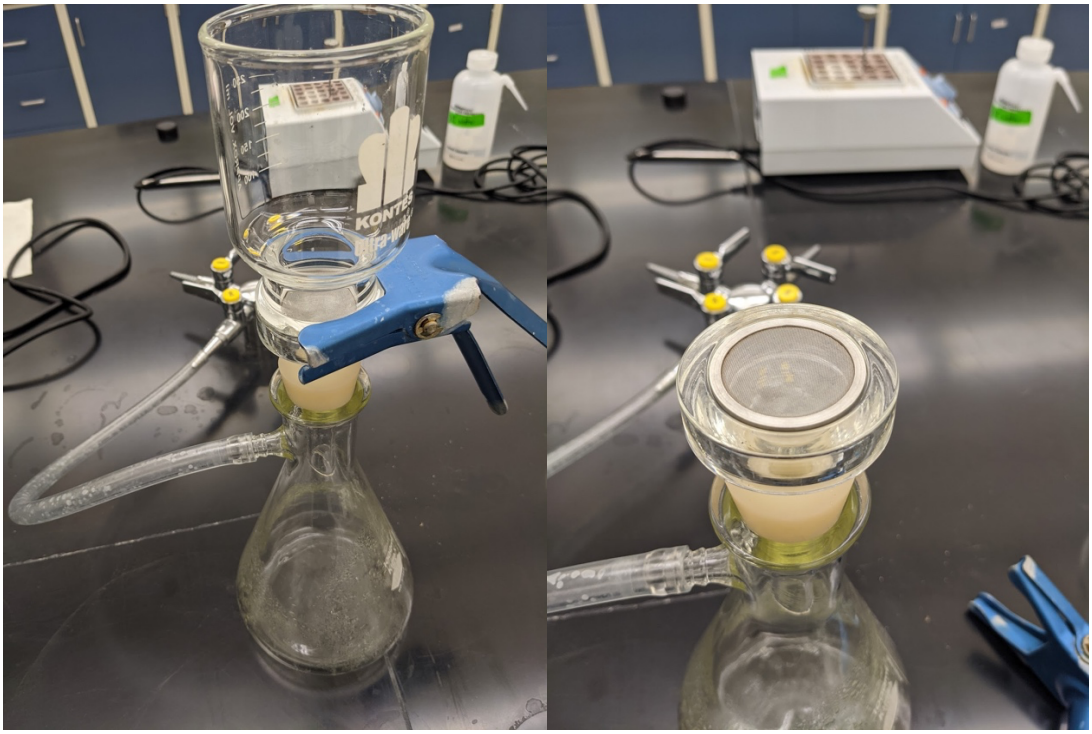


*Figure A.2-Filtration Setup*

26. Turn on the vacuum pump. The switch is on the west wall of the teaching lab.
27. Put the first filter on the screen using the tweezers. Open the vacuum valve.
28. Pipet the appropriate amount of sample through each filter (usually between 150 and 200 mL depending on the amount of visible solids and amount of available sample). You can pipet it directly onto the filter, or into a separate beaker that will be emptied through the filter. Rinse the beaker (if used to transfer) and sides of the intake above the filter with DI water to make sure no solids are left on the surfaces. Turn off the vacuum valve to remove the filter.
29. Repeat step 28 until there are three filters of mesophilic effluent and three with the thermophilic effluent (6 filters).
30. Place the filters in the 100°C oven for 1 hour.

31. Remove the filters and place them in the desiccator. Next, weigh each filter and record.
32. Place the filters in the 550°C oven for 20 minutes. Remove and place in the desiccator.
33. Weigh each filter and record.

** At some point during this process, the timer will go off for the COD. When this happens, perform the following steps.**

34. Remove all vials from the reactor and place in the red tray. Let them cool for 20 minutes.
35. Invert the vials a few times while still hot and put them back in the tray until they cool completely (about 40 minutes).
36. At the end of the cooling period, take them and a box of Kimwipes to the spectrophotometer for testing.
37. Click through the prompts on the spectrophotometer.
38. Clean off the first vial using a Kimwipe. Place it in the spectrophotometer and cover with the light seal.
39. Record the number that appears on the screen. Repeat with the remaining vials. If the readings are below the measurable range, the sample was diluted too much. The sample must be diluted more if the results are above the measurable range.

<u>Clean up:</u>

1. Rinse all used beakers and place with the dirty dishes to be washed.

2. Make sure the 550°C oven, reactor, spectrophotometer, pH probe, vacuum pump, and COD machine are turned off.

# APPENDIX B: SUPPLEMENTAL MATERIAL

Table B.0.1-Composition of Nutrient/Buffer Solution

| Compound | Formula Weight (g/mol) | Concentration in Stock Solution | Concentration in Nutrient Solution |
|---|---|---|---|
| **Stock Salts** | | (mg/L) | (mg/L) |
| $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ | 1236 | 68 | 0.03 |
| $Na_2B_4O_7\cdot 10H_2O$ | 381 | 45 | 0.02 |
| $NiCl_2\cdot 6H_2O$ | 238 | 90 | 0.04 |
| $MnCl_2\cdot 4H_2O$ | 198 | 158 | 0.07 |
| $CoCl_2\cdot 6H_2O$ | 238 | 90 | 0.04 |
| $ZnCl_2$ | 136 | 113 | 0.05 |
| $CuCl_2\cdot 2H_2O$ | 17 | 67 | 0.03 |
| $MgCl_2\cdot 6H_2O$ | 203 | 8,126 | 3.60 |
| $CaCl_2\cdot 2H_2O$ | 147 | 2,212 | 0.98 |
| $KHSO_4$ | 136 | 13,589 | 6.02 |
| | | | |
| **Ferric Chloride Stock** | | (g/L) | (mg/L) |
| $FeCl_3$ | 162 | 39.1 | 6.25 |
| | | | |
| **Spike Solution** | | (g/L) | (mg/L) |
| $NaNO_3$ | 85 | 67.9 | 679 |
| $NaH_2PO_4\cdot H_2O$ | 138 | 12.4 | 124 |
| | | | |
| **Buffer Solution** | | (g/L) | (mg/L) |
| $NaHCO_3$ | 84 | 17.7 | 202 |
| | | | |
| **Vitamin Solution** | | (mg/L) | (µg/L) |
| p-Aminobenzoic Acid | 137 | 10.0 | 1.14 |
| Biotin | 244 | 3.95 | 0.45 |
| Cyanocobalamin (B12) | 1355 | 0.18 | 0.02 |
| Folic Acid | 477 | 3.95 | 0.45 |
| Nicotinic Acid | 123 | 10.0 | 1.14 |
| Pantothenic Acid | 477 | 10.0 | 1.14 |
| Pyriodoxine HCl | 206 | 20.1 | 2.29 |
| Riboflavin | 376 | 10.0 | 1.14 |
| Thiamin HCl | 337 | 10.0 | 1.14 |
| Thioctic Acid | 206 | 10.0 | 1.14 |

# APPENDIX C: NUTRIENT SOLUTION CONTROLLER

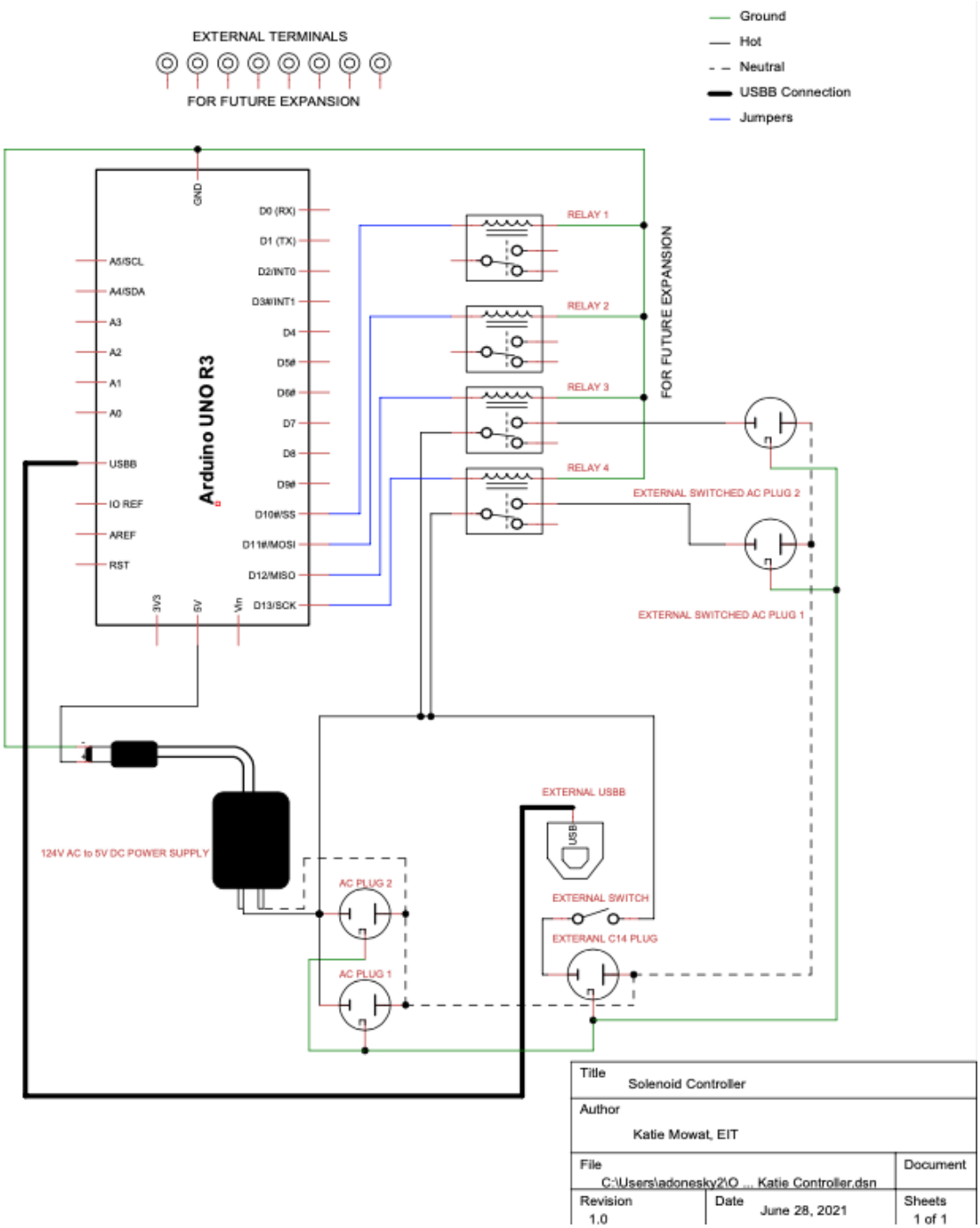



*Figure C.1-Schematic of Controller*

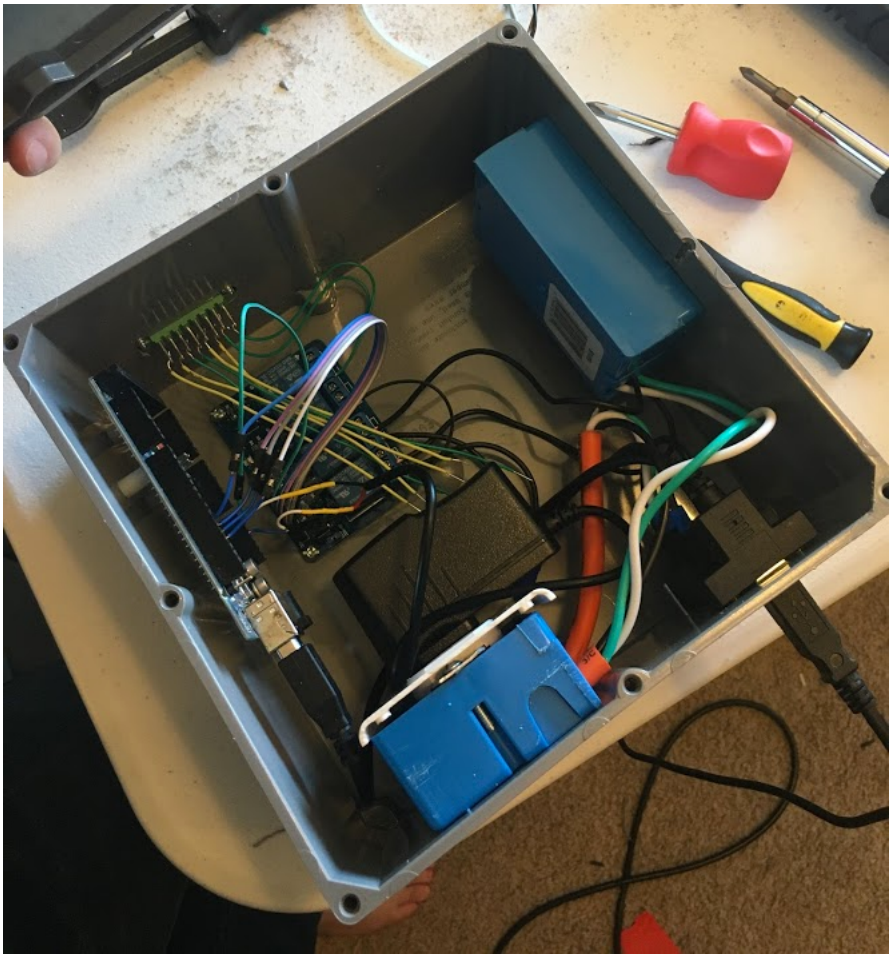


*Figure C.2-Inside of the Control Box*

# APPENDIX D: AQUEOUS TESTING RESULTS

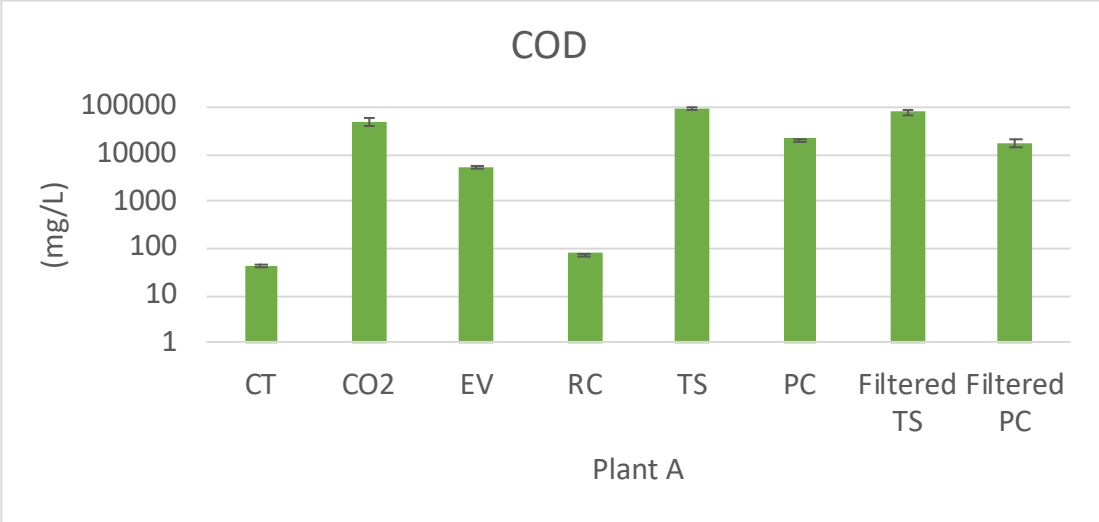



*Figure D.1-Chemical Oxygen Demand in Streams From Plant A*

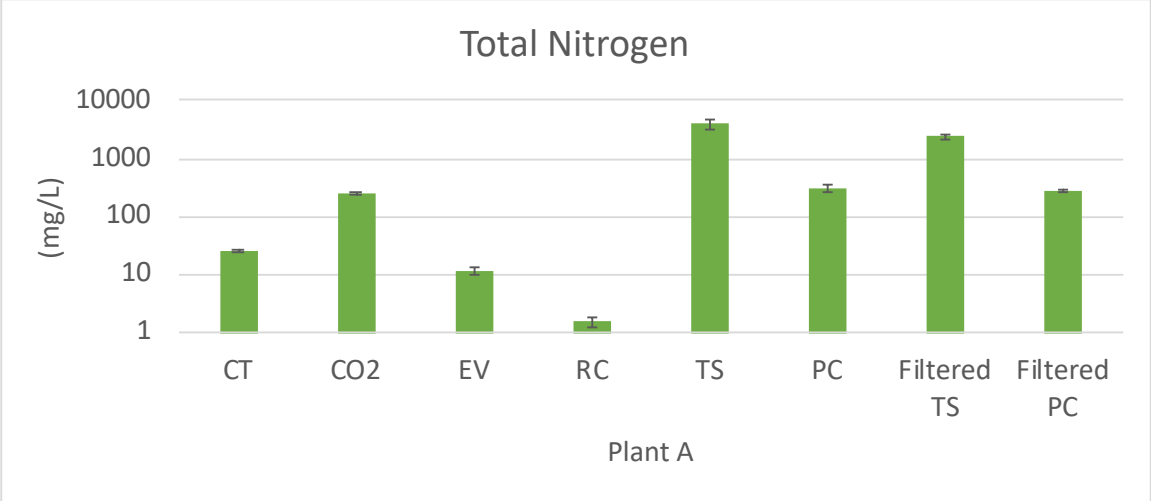



*Figure D.2-Total Nitrogen in Streams From Plant A*

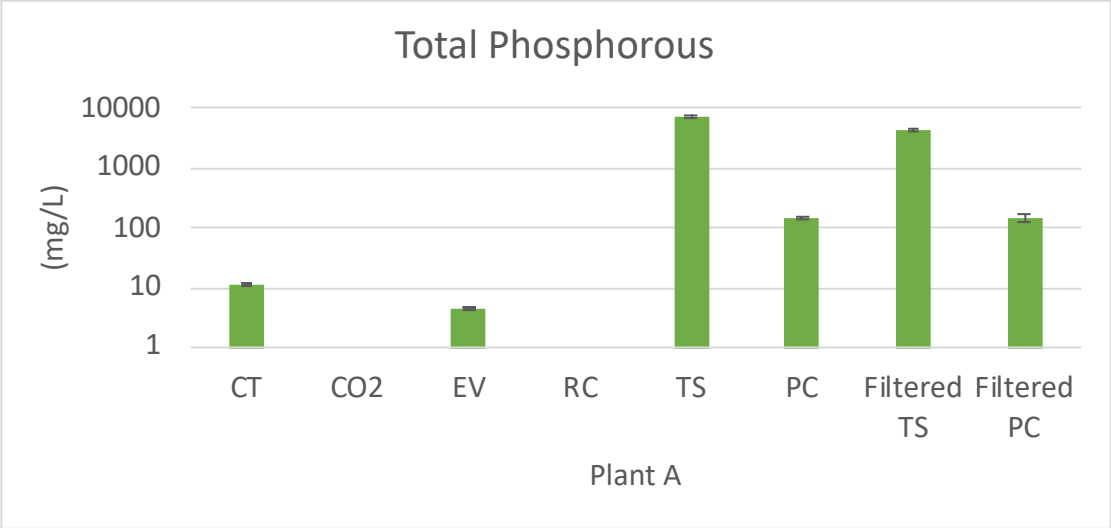



*Figure D.3-Total Phosphorous in Streams From Plant A*

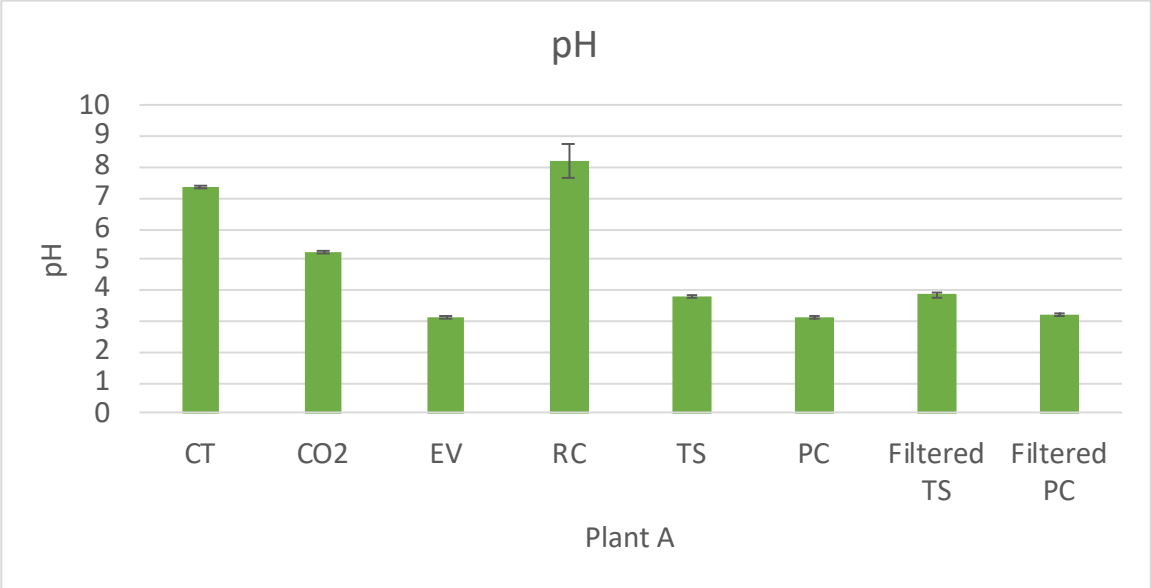



*Figure D.4-pH in Streams From Plant A*

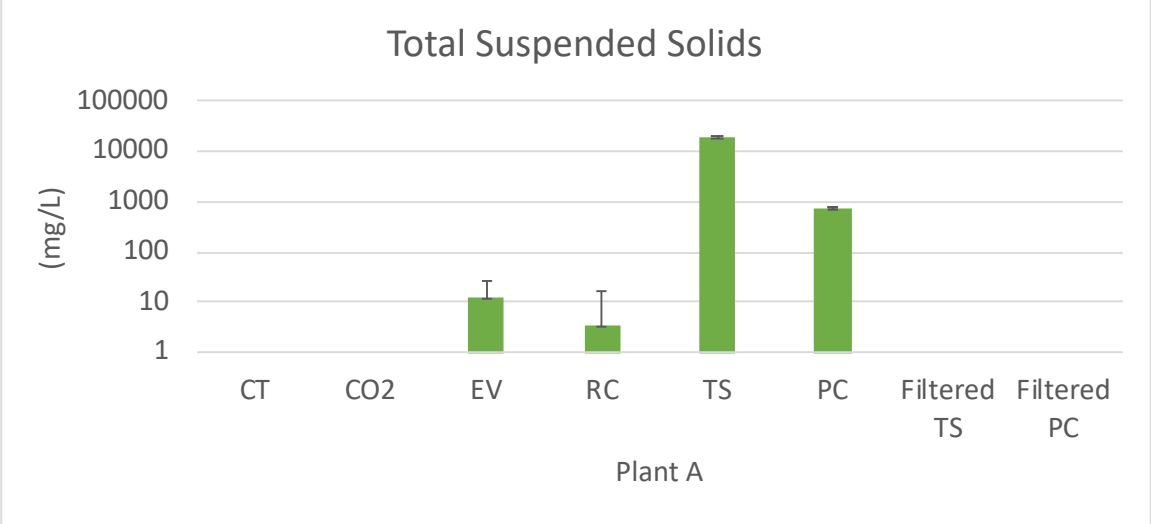



*Figure D.5- Total Suspended Solids in Streams From Plant A*

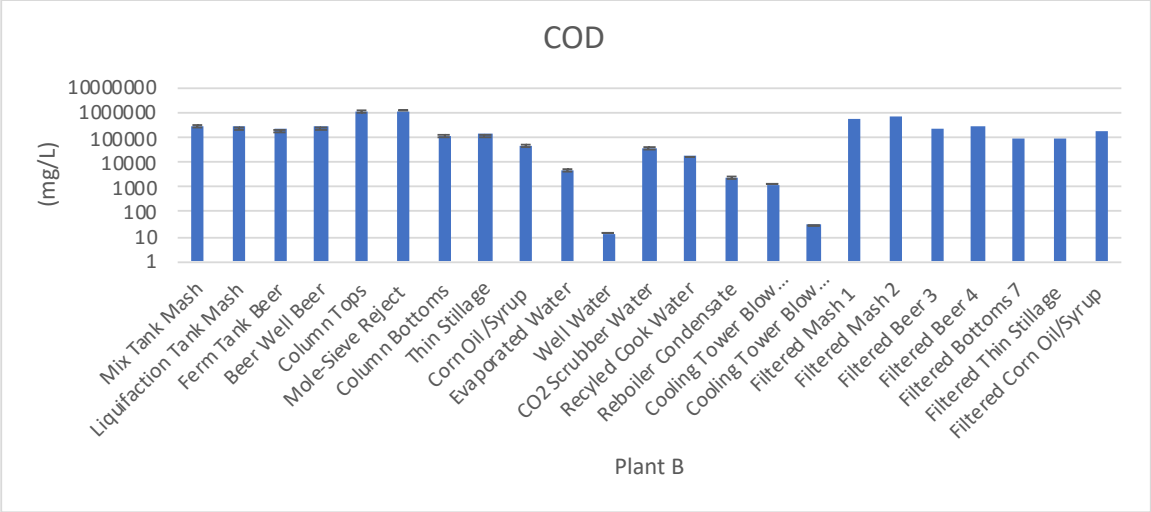



*Figure D.6-Chemical Oxygen Demand in Streams From Plant B*

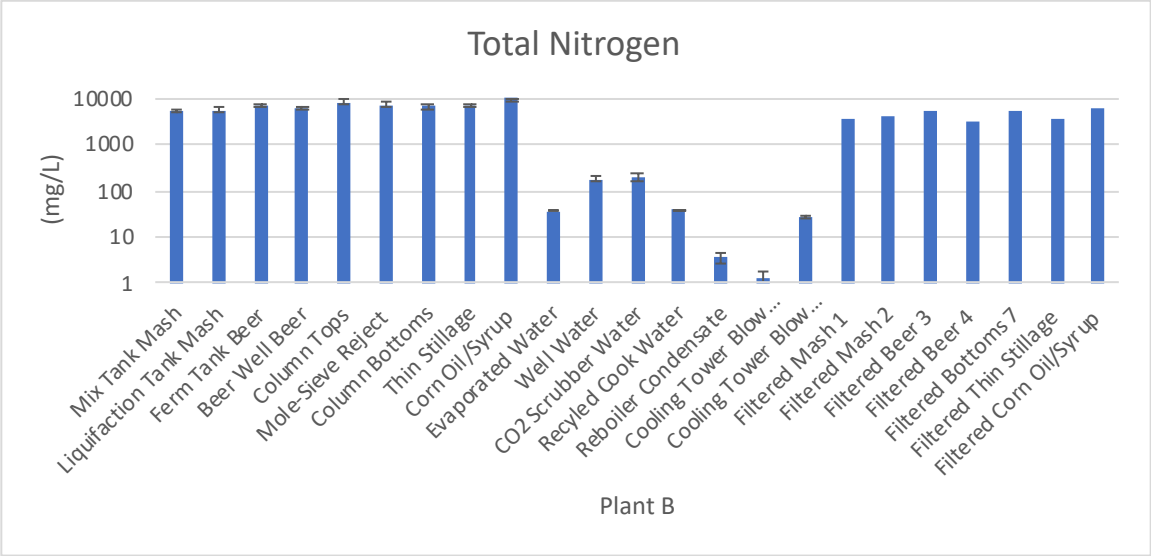



*Figure D.7-Total Nitrogen in Streams From Plant B*

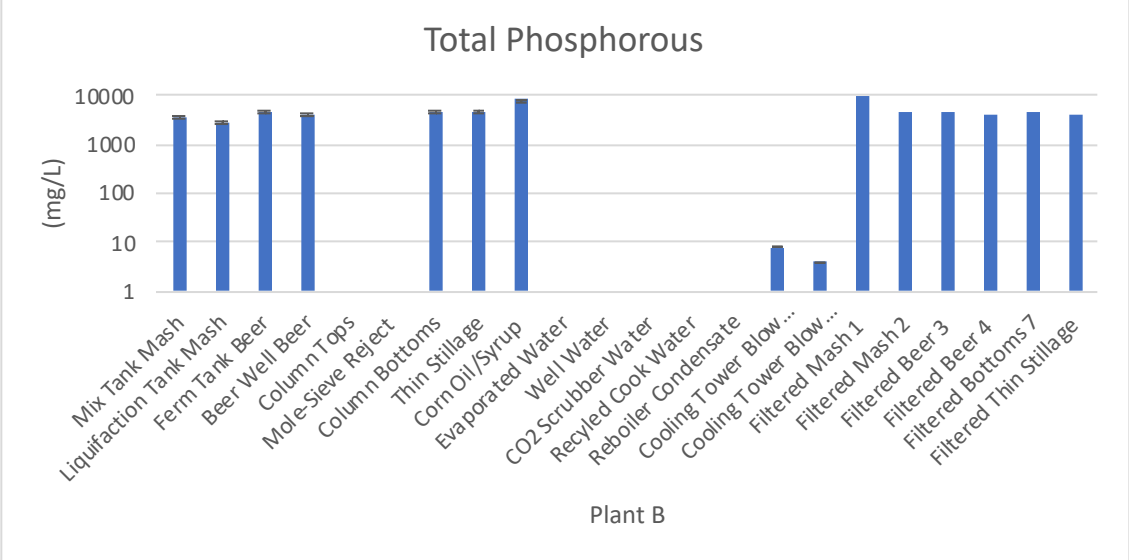



*Figure D.8-Total Phosphorous in Streams From Plant B*

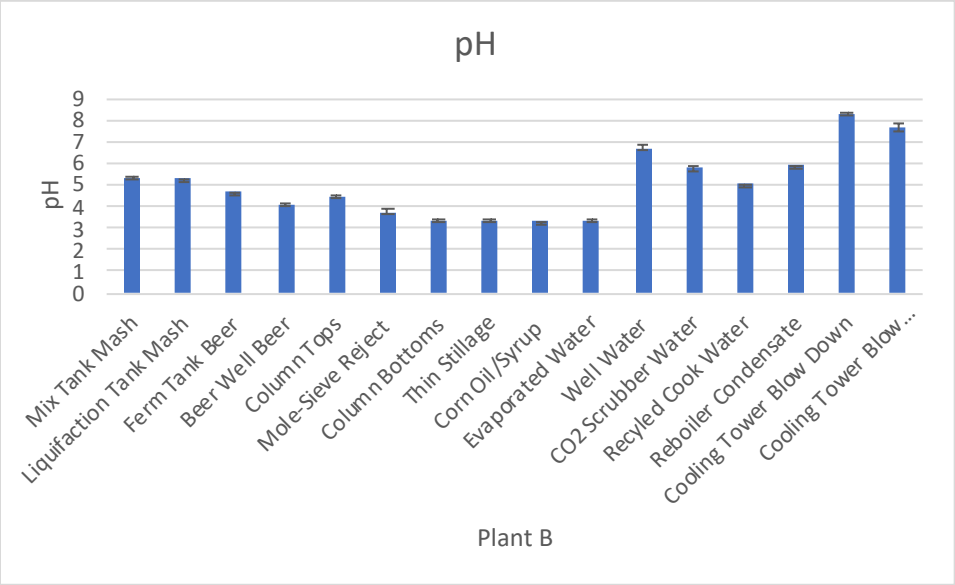



*Figure D.9-pH in Streams From Plant B*

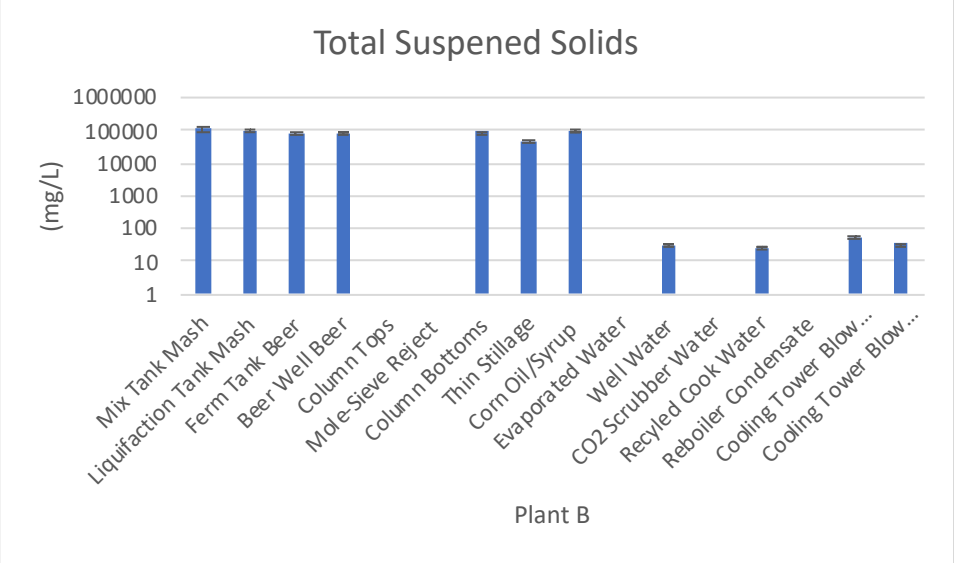



*Figure D.10-Total Suspended Solids in Streams From Plant B*

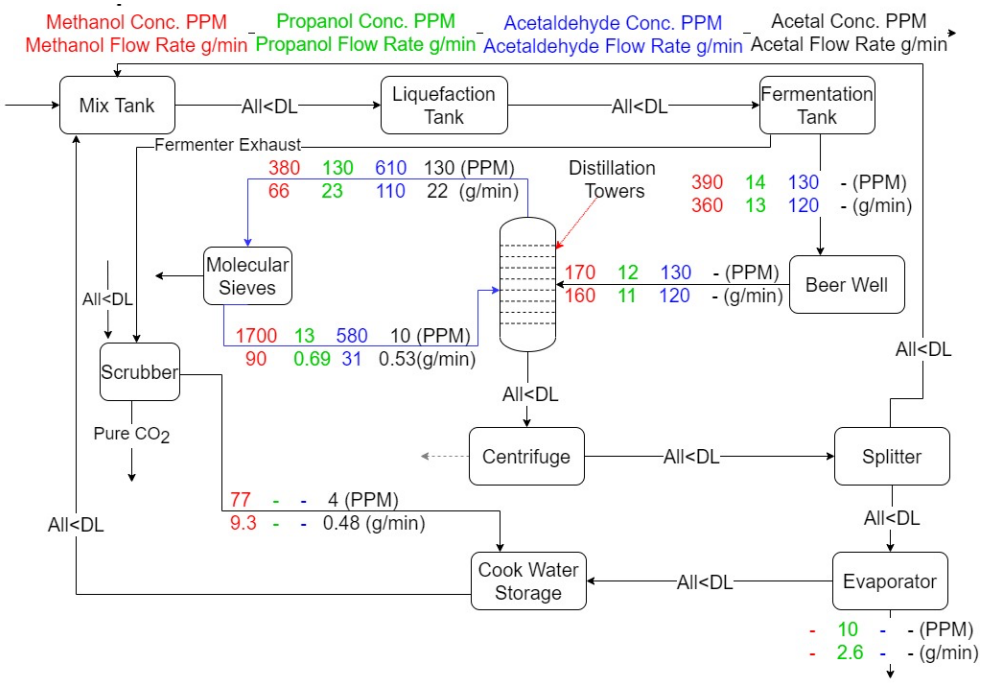



*Figure D.11-Plant B Impurities Concentration and Flow Diagram*

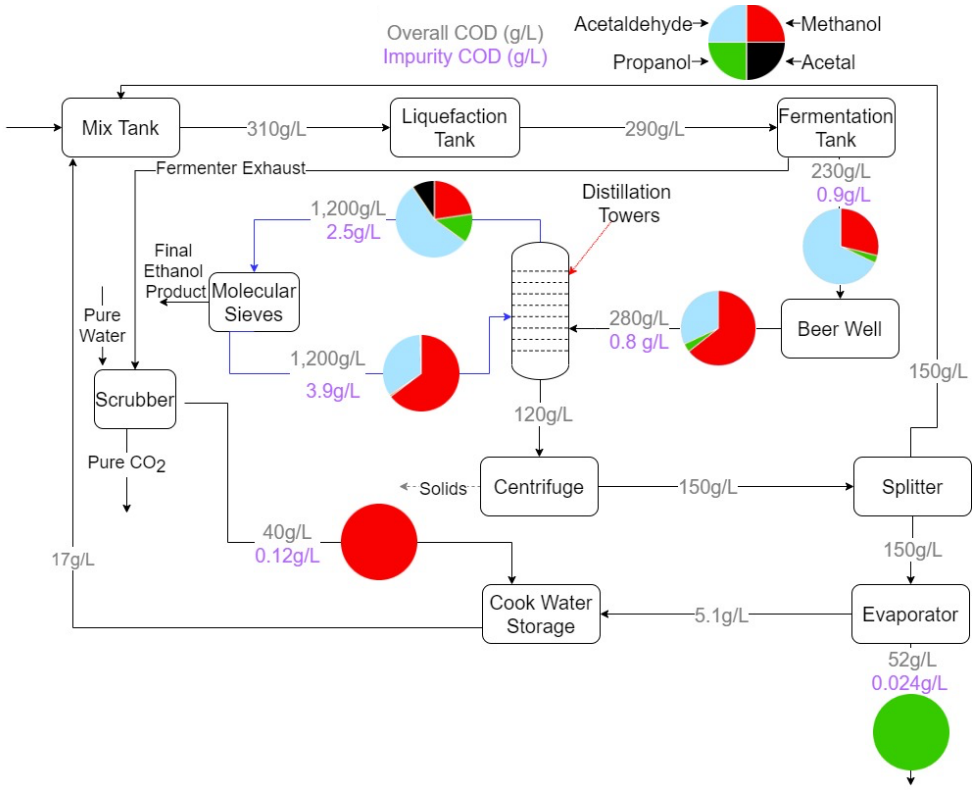
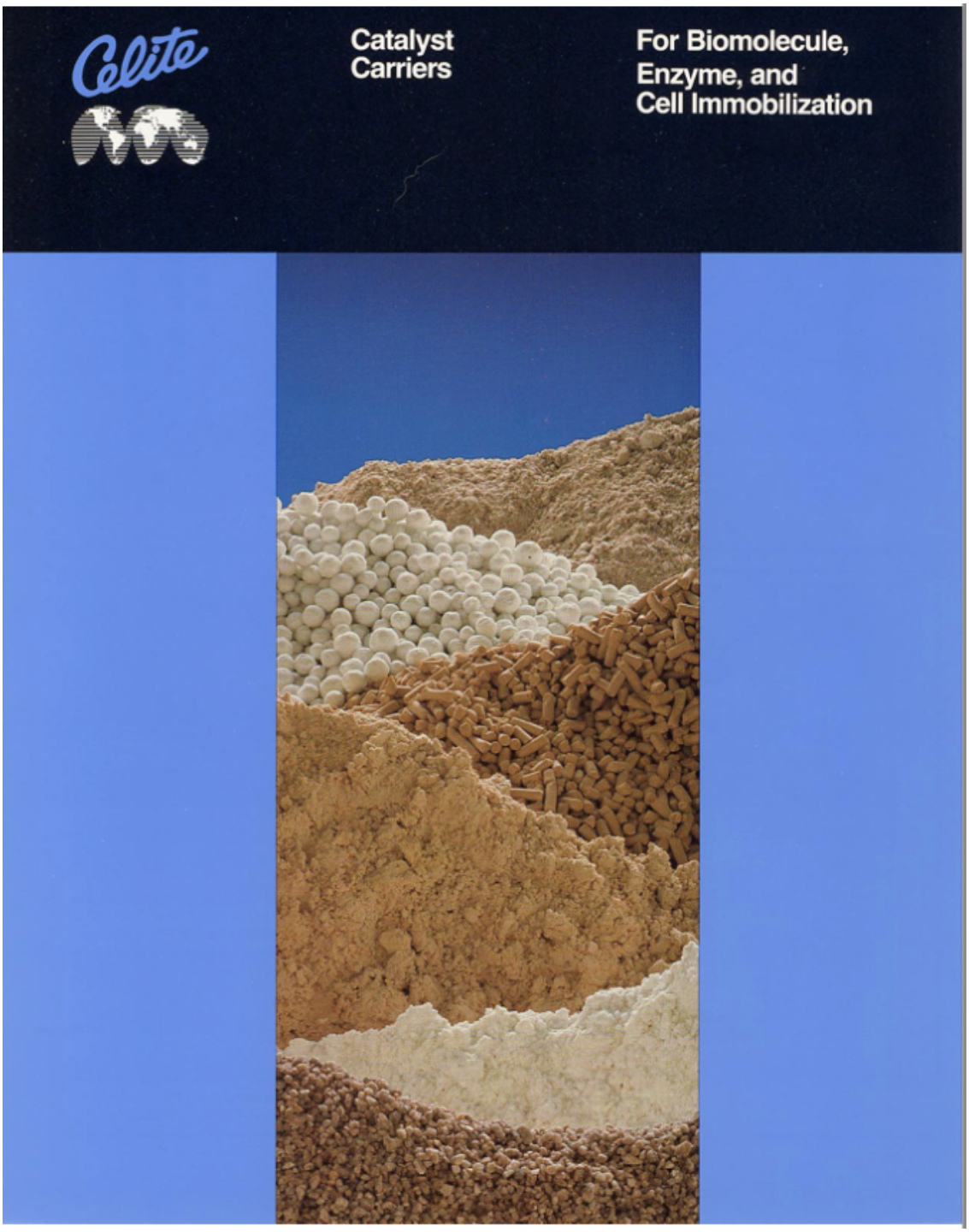



*Figure D.12-Impurities in Terms of COD*

# APPENDIX E: CATALYST CARRIER BROCHURE



# Celite® Catalyst Carriers For Biomolecule, Enzyme, and Cell Immobilization

The immobilization of enzymes and microbes for commercial production allow their use in continuous processes rather than traditional batch reactors. Although biocarriers can and are used in batch and semi-batch systems, the more economical continuous systems have the advantages of improved utilization of both the feed stocks and enzymes or cells and better process control in come cases.

The carriers most commonly required for large scale use are made of glass or ceramic materials. Celite has developed a series of these carriers designed expressly for the biotechnology industry. Their manufacture is based on more than fifty years of experience with silica and silicates. Celite also has experience with various types of fiber glass and ceramic materials.

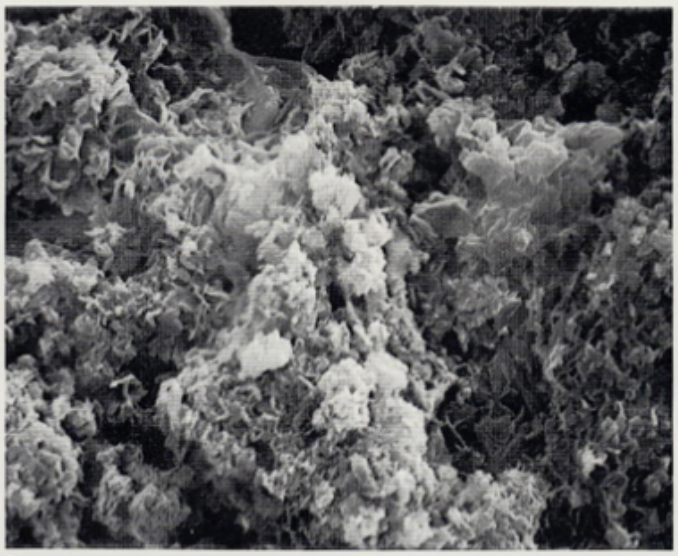
Immobilization requires closely-sized pores in the carriers. Properly-sized pores provide a number of advantages:

1. They maximize the concentration of the enzyme, biomolecule, or cell in the reactor.

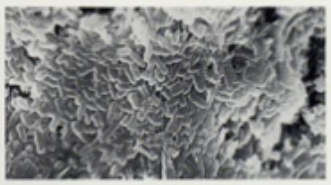
2. They protect the enzyme or cell from damaging fluid movement.

3. They help to protect the enzyme from destructive bacteria within the reactor system.

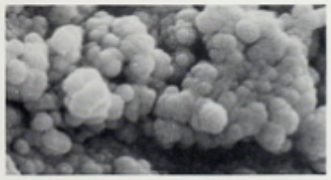
This series of catalyst carriers provides low-cost materials with controlled pore sizes. The low cost aspect makes many potential processes economical. Intended for use in pharmaceuticals, chemicals, waste disposal and many other applications, these carriers provide the combination of properties necessary for an efficient operation.



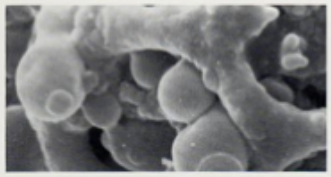
Scanning electron micrograph of typical enzyme carrier pore structure magnification.



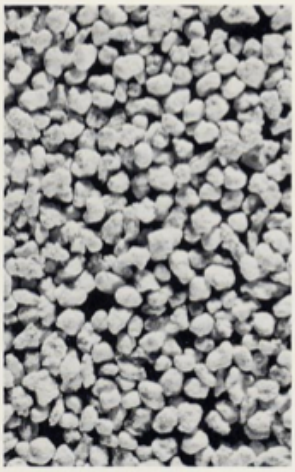
Bacterial cells immobilized on Celite proprietary controlled porosity carrier.

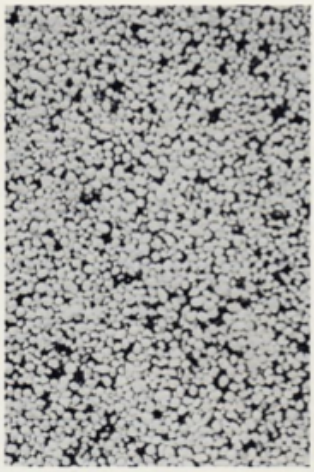


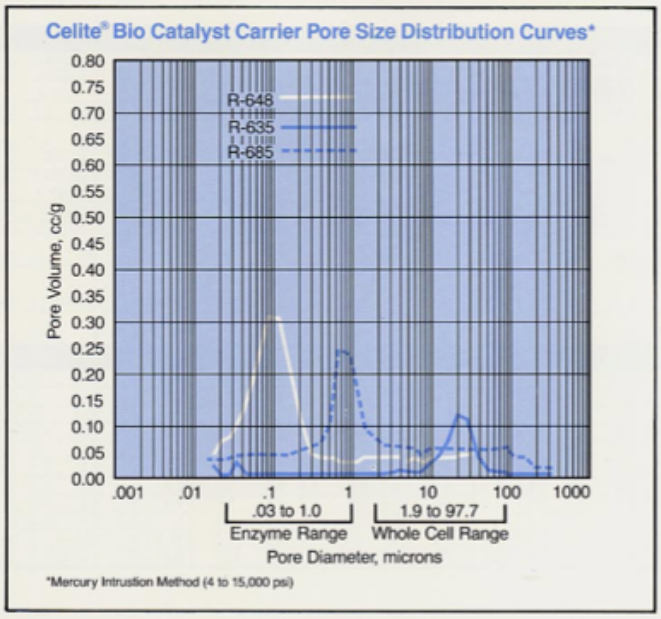
Hybridoma cells immobilized within and on Celite engineered porosity matrix.



Yeast cells immobilized within Celite carrier for continuous processing.






Celite® Bio Catalyst Carrier Pore Size Distribution Curves*
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Pore Volume, cc/g
R-648
R-635
R-685
.001
.01
.1
1
10
100
1000
.03 to 1.0
1.9 to 97.7
Enzyme Range
Whole Cell Range
Pore Diameter, microns
*Mercury Intrusion Method (4 to 15,000 psi)

The carriers shown in this brochure are just an example of our capabilities. There are very few standard processes in the biotechnology field and, therefore, custom-made products for specific applications must be considered. Celite will work with individual customers in developing carriers best suited for specific applications. Information on alternatives in selecting pore sizes and volumes, carrier strength, sizes and shapes can be supplied.

### Carrier Selection

Selecting a carrier involves defining the properties which are most important in the carrier. Typically, pore diameter and volume, strength, chemical inertness and carrier shape are most critical. These and other properties are interrelated and compromises can be made to produce the most economical carrier.

### Pore Diameter

Production rates are greatly affected by the concentration of the enzymes or microbes and by the ease of diffusion to them. It has been found that by maximizing the concentration and accepting the resulting diffusion rates gives the best performance. The highest loadings are obtained when the pore diameters are based on the enzyme or microbe diameters. Pores which are one to ten times the size of the largest involved element typically provide the highest production rates.

In whole cell immobilization, the pore diameters are based on the major cell dimensions. Living systems require additional care to insure adequate space for cell reproduction. Typically, diameters of 1 to 50 microns are needed to accommodate the cells.

In enzyme processes, the desired pore diameter is based either on the enzyme's molecular weight or possibly on the dimensions of the reacting organic molecules. The desired diameters are usually between 200 and 2000 Angstroms.

### Pore Volume

The pore volume is very important since it indicates the volume available for microbes to occupy. Specifically, only the volume of the pores within the useful size range should be considered. High pore volumes maximize the concentration per volume in the reactor. Although the pore volume can be controlled, there are trade-offs with other carrier properties, especially the carrier hardness.

### Surface Area

The surface area is an indication of the number and shape of the carriers' pores and a measure of the available enzyme or molecular bonding sites. A high surface area is expected in a small pore carrier. The small pore carriers, such as Celite 640 and Celite 650, have surface areas of over 60 square meters per gram. The microbe carriers have relatively low surface areas but large pore diameters and volumes to allow better biomass accumulation.

### Hardness

The mechanical strength of the carrier is determined by the composition, production process and physical size. The porosity of the carrier very signficantly affects its strength. Increases in pore volume have a large negative impact on particle strength. A minimum acceptable strength should be established for a given application, thereby allowing the optimization of the carrier's remaining properties.

### Particle Size

Celite catalyst carriers can be produced in several forms: powder, pellet and sphere. The shape of these carriers can be custom fabricated in sizes ranging from 1.0 to 10 millimeters in diameter.

Diffusion limitations in reaction processes often require smaller particle sizes. The more commonly used carriers are in the range of 0.3 to 1.0 millimeters. However, powders can be produced in the micron range.

### Chemical Composition

Celite catalyst carriers are made of rigid, inorganic materials. These materials provide the advantages of thermal and chemical stability, mechanical strength and rigidity and microbial resistance.

Diatomite, one of the basic raw materials, is compatible with a very wide range of aqueous and organic environments. It is currently used in the filtration of drugs, pharmaceuticals, beverages, acids and petrochemicals. Although each individual application must be considered separately, Celite catalyst carriers are recommended wherever high-silica glass is appropriate.

Typical physical properties and chemical analysis for our standard catalyst carriers are shown below.

These concepts are the basis for the selection of an immobilization carrier. They are to be considered as general guidelines in determining the parameters required for specific applications. Our technical staff can aid you in the selection of the most appropriate carrier.

Materials carriers can also be custom-tailored to meet your specific enzyme and microbe immobilization needs. Contact Celite Biochemistry Products & Services for additional information, samples and recommendations with regard to carrier requirements.

## Typical Physical Properties

| Product | R-600 | R-625 | R-630 | R-631 | R-632 | R-633 | R-634 | R-635 | R-640 | R-646 | R-647 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Form | pellet (1/8") | pellet (1/8") | sphere (3/8) | sphere (8/14) | sphere (14/30) | sphere (30/50) | sphere (50/100) | pellet .25"D x .50"L | pellet (1/8") | sphere (8/14) | sphere (14/30) |
| Mean Pore Diameter, μ | 0.38 | 5.5 | 6.6 | 6.0 | 7.0 | 6.5 | 5.0 | 20 | 0.03 | 0.04 | 0.07 |
| Surface Area, B.E.T., $m^2/g$ | 19 | 12.4 | 1.3 | 1.0 | 2.0 | 1.3 | 2.1 | 0.27 | 61 | 45 | 51 |
| Total Pore Volume, cc/g | 0.938 | 0.74 | 1.45 | 1.45 | 1.19 | 1.47 | 1.08 | 0.61 | 0.76 | 0.8701 | 0.9723 |
| Volume Fraction 400-1000 A, cc/g | 0.072 (7.7%) | 0.004 (0.5%) | 0.008 (0.5%) | 0.003 (0.2%) | 0.006 (0.5%) | 0.008 (0.5%) | 0.005 (0.5%) | | 0.099 (13.0%) | 0.1690 (19.4%) | 0.1759 (18.2%) |
| Volume Fraction 1.0-50μ, cc/g | 0.086 (9.2%) | 0.669 (94.4%) | 1.362 (94.0%) | 1.322 (91.3%) | 1.096 (92.0%) | 1.424 (96.2%) | 1.030 (95.4%) | 0.513 (83.6%) | 0.065 (8.6%) | 0.1239 (14.2%) | 0.2213 (22.8%) |
| Water Absorption, % by weight, pellet method | 100.8 | 86 | 170 | 60 | 84 | 240 | 210 | 60 | 93 | 159 | 163 |
| Crush Strength — Monsanto Hardness Test, kg | 1.8 | 1.6 | 1.3 | 61-69† | 15-24† | 27-28† | 0-5† | 8 | 2.2 | 5† | 4.7† |
| Bed Density (compacted) lbs/$ft^3$ | 26 | 32 | 21 | 17 | 20 | 22 | 24 | 32 | 29 | 25 | 24 |

## Typical Chemical Analysis %

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 84.6 | 84.8 | 88.2 | 88.2 | 88.2 | 88.2 | 88.2 | 82.3 | 87.0 | 87 | 87 |
| $AL_2O_3$ | 7.5 | 6.4 | 3.5 | 3.5 | 3.5 | 3.5 | 3.5 | 7.2 | 6.1 | 6.1 | 6.1 |
| CaO | 0.9 | 1.7 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 2.6 | 0.9 | 0.9 | 0.9 |
| MgO | 1.0 | 1.1 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 1.2 | 0.8 | 0.8 | 0.8 |
| $FE_2O_3$ | 1.7 | 2.1 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.9 | 1.6 | 1.6 | 1.6 |
| $Na_2O$ | 1.1 | 2.7 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 | 3.3 | 1.2 | 1.2 | 1.2 |
| $K_2O$ | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.9 | 0.4 | 0.4 | 0.4 |
| $P_2O_5$ | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.4 | 0.1 | 0.1 | 0.1 |
| $TiO_2$ | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| LOI | 2.1 | 0.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 12.3 | 2.1 | 2.1 | 2.1 |
| pH of slurry | 9.4 | 10.0 | 9.8 | 9.5-10.5 | 9.5-10.5 | 10.4 | 9.5-10.5 | 8.0* | 8.9 | 8.5-9.0 | 8.5-9.0 |

* Buffered slurry
† Hardness, % fines produced by 100 psi load

## Typical Physical Properties

| Product | R-648 | R-649 | R-650 | R-660 | R-670 | R-675 | R-680 | R-681 | R-682 | R-685 | R-690 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Form | sphere (30/50) | sphere (50/100) | pellet (1/8") | pellet (1/8") | pellet (1/4") | pellet (1/8") | powder | powder | powder | powder | pellet (1/8") |
| Mean Pore Diameter, μ | 0.14 | 0.25 | 0.05 | 0.05 | 0.4 | 0.05 | 1.8 | 4.0 | 1.8 | 2.0 | 0.19 |
| Surface Area, B.E.T., $m^2/g$ | 46 | 39 | 88 | 116 | 25 | 71 | 105 | 2.5 | 5.6 | 175 | 85 |
| Total Pore Volume, cc/g | 1.186 | 0.7844 | 0.71 | 0.464 | 0.64 | 0.511 | 5.47 | 3.23 | 2.83 | 5.53 | 0.432 |
| Volume Fraction 400-1000 A, cc/g | 0.0234 (19.7%) | 0.1654 (21.1%) | 0.120 (16.8%) | 0.057 (12.4%) | 0.060 (9.4%) | 0.338 (65.0%) | 0.666 (12.1%) | 0.003 (0.1%) | 0.019 (0.7%) | 0.45 (8.1%) | 0.050 (11.6%) |
| Volume Fraction 1.0-50μ, cc/g | 0.394 (33.2%) | 0.1632 (20%) | 0.049 (6.9%) | 0.012 (2.6%) | 0.002 (0.3%) | 0.002 (0.3%) | 3.023 (55.3%) | 3.117 (96.6%) | 2.347 (82.8%) | 0.65 (11.8%) | 0.024 (5.5%) |
| Water Absorption, % by weight, pellet method | 160 | 160 | 80 | 63 | 62 | 64 | 480 | 250 | 190 | Hydrophobic | 62 |
| Crush Strength — Monsanto Hardness Test, kg | 4.1† | 0.3† | 3.5 | 6 | 7 | 7 | N/A | N/A | N/A | N/A | 2.3 |
| Bed Density (compacted) lbs/$ft^3$ | 25 | 25 | 30 | 38 | 34 | 38 | 8 | 11 | 13 | 17 | 39 |

## Typical Chemical Analysis %

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 87.0 | 87 | 85.1 | 63.9 | 85.1 | 59.9 | 57.3 | 93.6 | 92.9 | 63.9 | 54.0 |
| $AL_2O_3$ | 6.1 | 6.1 | 7.0 | 3.1 | 7.5 | 6.4 | 2.9 | 2.3 | 3.2 | 3.1 | 35.0 |
| CaO | 0.9 | 0.9 | 0.9 | 0.4 | 0.8 | 16.3 | 25.7 | 0.2 | 0.3 | 0.4 | 0.6 |
| MgO | 0.8 | 0.8 | 0.9 | 14.8 | 0.9 | 1.0 | 0.7 | 0.5 | 0.6 | 14.8 | 0.9 |
| $FE_2O_3$ | 1.6 | 1.6 | 1.7 | 1.5 | 1.7 | 1.4 | 0.8 | 0.8 | 1.1 | 1.5 | 1.5 |
| $Na_2O$ | 1.2 | 1.2 | 1.3 | 0.1 | 0.9 | 0.7 | 0.2 | 2.3 | 0.5 | 0.1 | 0.5 |
| $K_2O$ | 0.4 | 0.4 | 0.6 | 0.5 | 0.5 | 0.4 | 0.5 | 0.4 | 0.7 | 0.5 | 0.4 |
| $P_2O_5$ | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.5 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 |
| $TiO_2$ | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 |
| LOI | 2.1 | 2.1 | 2.2 | 13.0 | 2.3 | 10.6 | 10.6 | 0.4 | 0.9 | 13 | 6.1 |
| pH of slurry | 8.5-9.0 | 8.5-9.0 | 7.9 | 9.9 | 7.4 | 9.7 | 8.8 | 10.1 | 6.6 | 7.4 | 8.5 |

* Buffered slurry
† Hardness, % fines produced by 100 psi load