Author: **Schmick, Matthew, J**
Title: ***Dry Hopping and its Effect on Beer pH***

The accompanying research report is submitted to the **University of Wisconsin-Stout**, **Graduate School** in partial completion of the requirements for the

Graduate Degree/ Major: MS Food and Nutritional Sciences

Research Advisor: Carol Seaborn, Ph.D., RD, CD

Submission Term/Year: Spring, 2014

Number of Pages: 53

Style Manual Used: American Psychological Association, 6th edition

☒ **I understand that this research report must be officially approved by the Graduate School and that an electronic copy of the approved version will be made available through the University Library website**
☒ **I attest that the research report is my original work (that any copyrightable materials have been used with the permission of the original authors), and as such, it is automatically protected by the laws, rules, and regulations of the U.S. Copyright Office.**
☒ **My research advisor has approved the content and quality of this paper.**

STUDENT:

NAME Matthew Schmick **DATE:**

ADVISOR: (Committee Chair if MS Plan A or EdS Thesis or Field Project/Problem):

NAME Carol Seaborn **DATE:**

This section for MS Plan A Thesis or EdS Thesis/Field Project papers only
Committee members (other than your advisor who is listed in the section above)

1. **CMTE MEMBER'S NAME:** **DATE:**

2. **CMTE MEMBER'S NAME:** **DATE:**

3. **CMTE MEMBER'S NAME:** **DATE:**

This section to be completed by the Graduate School
This final research report has been approved by the Graduate School.

Director, Office of Graduate Studies: **DATE:**

Schmick, Matthew J. ***Dry Hopping and its Effect on Beer pH***

Abstract

Dry hopping is a method to add large amounts of hop flavor and aroma into beer that otherwise cannot be added. The purpose of this study was to determine the effect that dry hopping beer has on finished beer pH. Four commercial beers and six hop varieties were used to determine the effect on finished beer pH, if there was any correlation between the hop attributes analyzed and the pH change during dry hopping, and whether there was a correlation between the beer attributes analyzed and the pH change during dry hopping. It was determined that there is an increase in beer pH during the dry hopping process. Results showed that a mean pH increase of between pH 0.040 ± 0.003 and 0.056 ± 0.006 at a rate equivalent to 0.5 lb./bbl. of dry hops added. When adding dry hops equivalent to 3.0 lbs./bbl. there was a mean pH increase of pH 0.233 ± 0.022 and 0.332 ± 0.031. There was no significant correlation between the hop attributes analyzed and the increase in beer pH during dry hopping, and there was no significant correlation between the beer attributes analyzed and the increase in beer pH during dry hopping.

Acknowledgments

First off, I sincerely would like to thank Dr. Eun Joo Lee for taking on a project with a student that she did not even know. Her ability to meet with me while I lived hours away and her wonderful assistance during my research allowed me to get to this point.

I would also like to thank Dr. Carol Seaborn for her utmost understanding in my goal of finishing this research project. Without her ability to take on a topic that she was not familiar with at the time and jump right in tells me that she is in the profession of teaching for the right reasons. For her to see that I am capable of finishing such a degree means a lot to me.

I would also like to thank my family for their continued support throughout this long process, and last but not least I would like to thank the love of my life Jessica. Without her supporting me 100% I would have not been able to do what I set out to do many years ago. Her support has been more than anyone could ask for, and I will forever be indebted to her.

Table of Contents

.... Page

Abstract 2

List of Tables 7

List of Figures 8

Chapter I: Introduction 9

Statement of the Problem 10

Purpose of the Study 10

Assumptions of the Study 11

Definition of Terms 11

Limitations of the Study 12

Chapter II: Literature Review 14

The Brewing Process 14

Hop History 15

Hop Chemistry 17

Alpha and Beta Acids 17

Essential Oils 18

Polyphenols 21

Isomerization 22

Dry Hopping Techniques 22

pH and the Role it Plays in Finished Beer 24

Physical Stability 24

Flavor Effects 24

Beer Spoiling Microorganisms 25

Chapter III: Methodology 27

Sample Selection and Description 27

Sample Preparation 28

pH Analysis of Beer 29

Determination of Beer Color 29

Determination of Final Beer Specific Gravity 29

Total Beer Acidity Analysis 29

pH Analysis of Hops 30

Ash Analysis of Hops 30

Water Activity Analysis 31

Bench Top Dry Hopping 31

Data Analysis 32

Chapter IV: Results and Discussion 33

Beer Analysis 33

Beer Color 34

Beer Acidity 34

Specific Gravity 34

Beer pH 35

Hop Chemistry 35

Water Activity of Hops 36

pH of Hops 36

Percent Ash of Hops 37

pH Values per Hop Dose 37
Dry Hop Analysis 41
Correlation Between Hop Chemistry Analysis and pH Increase 45
Correlation Between Beer Chemistry Analysis and pH Increase 45
Chapter V: Conclusion 46
Limitations 47
Recommendations 48
References 50

List of Tables

Table 1: Chemical Compounds and Associated Aroma from a Variety of Hop Essential Oils ... 20

Table 2: Chemistry Analysis of Four Commercially Available Beers 33

Table 3: Chemistry Analysis of Six Hop Varieties... 36

Table 4: Mean pH Increase of Four Commercial Beers from Six Hop Varieties at an Equivalent Dry Hop Dose Rate of 0.5 lb./bbl. 42

Table 5: Mean pH Increase of Four Commercial Beers from Six Hop Varieties at an Equivalent Dry Hop Dose Rate of 3.0 lb./bbl 43

Table 6: Mean pH Increase of Four Commercial Beers at an Equivalent Dry Hop Dose Rate of 3.0 lbs./bbl.. 44

List of Figures

Figure 1: Chemical structure of alpha acids and beta acids 18

Figure 2: Chemical structure of hydrocarbon components of hop essential oils) 19

Figure 3: Isomerization of alpha acids 22

Figure 4: Hop sample after grinding 28

Figure 5: Beer being degassed for preparation for dry hopping 28

Figure 6: Hop slurry for pH analysis 30

Figure 7: Dry hops mixing on an orbital shaker 32

Figure 8: Color of beer samples 34

Figure 9: Mean pH values for Commercial Beer A (CBA) after dry hopped 38

Figure 10. Mean pH values for Commercial Beer B (CBB) after dry hopped 39

Figure 11: Mean pH values for Commercial Beer C (CBC) after dry hopped 40

Figure 12: Mean pH values for Commercial Beer D (CBD) after dry hopped 41

Chapter I: Introduction

The Brewers Association defines a craft brewery as one that is small, independent, and traditional (Brewers Association, 2013). More specifically, this means annual production is less than six million barrels per year with less than 25% of the craft brewery owned or controlled by an alcoholic beverage industry member who is not a craft brewer (Brewers Association, 2013). Lastly, traditional is defined as a brewer having either an all malt flagship brand or at least 50% of the volume in either all malt beers or in beers that use adjuncts to enhance flavor rather than lighten flavor (Brewers Association, 2013). As of June 30, 2013, there are 2,538 breweries operating in the United States. Of those breweries, 2,483 of them are craft breweries. This is the greatest number of breweries in the United States since Prohibition (Brewers Association, 2013).

With the popularity of craft beer and brewery competition on the rise, breweries are looking for superior ways to add more flavor and aroma into their beers. One method of adding flavor and aroma is called dry hopping. Hops are the female flowers or seed cones of the hop plant used to add bitterness, flavor, and aroma to beer. Dry hopping is a technique used to add more hop flavor and aroma into beer by introducing hops to a fermenter, bright beer tank, or cask (Hieronymus, 2012).

Each brewer has a unique way of dry hopping and will add a different amount of hops, dry hop at different temperatures, and have different hop residency times. With craft breweries focusing on strengthening the hop flavor in their beers, the volume of hops used throughout the cold side of the brewing process has increased from historical standards (Steele, 2012). Brewers are aware that adding too many hops for dry hopping can negatively effect the flavor of the beer with vegetable-like or fishy flavors (Hieronymus, 2012).

There has been little information published on the negative effects of large hop additions during dry hopping. One issue not yet explored is the effect dry hopping could have on the final pH of finished beer. A standard finished beer pH will be between 4.0 and 4.5 (Strong, 2011). If the pH is at 4.6 or above, there could be possible negative side effects that would be detrimental to the beer quality, including microbial stability and off-flavor/drinkability concerns (Strong, 2011). Along with microbial and flavor concerns, the beer appearance could suffer as well (Baxter & Hughes, 2001).

Statement of the Problem

With the increase of craft breweries throughout the United States, craft brewers are looking to stand out in the industry by adding more hops into their beers. With very few studies conducted on the negative effects of large dry hop additions, this research will examine one aspect of possible undesirable side effects. The change in pH in relationship to the quantity and variety of hops and variety of beer styles during dry hopping will be researched. Discovering whether dry hopping effects the final pH of beer will assist brewers in producing the most flavorful hopped beers possible without negative side effects.

Purpose of the Study

The purpose of this study was to determine whether or not dry hopping beer would affect the final pH of the beer. The main objectives of this study were to:

1. Determine if dry hopping effects the pH of the finished beer.
2. If there is a change in the pH of beer due to dry hopping, determine if the effect of the changing pH is hop specific and/or beer style specific.
3. If there is a change in the pH of beer due to dry hopping, determine if there is a correlation between the analyzed hops chemistry and pH change due to dry hopping

and if there is a correlation between the analyzed beer chemistry and pH change due to dry hopping.

Assumptions of the Study

It was assumed that the alpha acid content of the hop samples used in this study were accurate according to the manufacturer and the alpha acid content did not degrade during the study.

Definition of Terms

Alpha acid. A type of soft resin in the hop plant that is absorbed by the wort before the addition of yeast during the boiling process and provides the primary bitterness to beer. Alpha acid content is reported for each hop crop as a percentage of the total weight of the hop cone (Janson, 1996).

Dry hopping. Hops used after wort boiling to provide hop aromatic flavors. Dry hopping provides more aromatics than aromatic (finishing) hops because the hop oils are never exposed to boiling water (Janson, 1996).

EBC. European Brewery Convention. A system for analyzing color intensity in beer using a spectrophotometer at a wavelength of 430 nm using a one cm cuvette (Chester F. Carlson Center for Imaging Science, 2008).

Head retention. The foam stability of a beer as measured in seconds by time required for a 1-inch foam collar to collapse (Craft Beer, 2014).

Hops (hop cones). Flowers of the female hop plant *Humulus lupulus*, originally used as a preservative for beer. Hops provide primary bitterness to beer as well as aroma and other flavors. A wide variety of hops are available, each offering its own bitterness and flavor characteristics (Janson, 1996).

Kilning. The process of heat-drying malted barley in a kiln to stop germination and to produce a dry, easily milled malt from which the brittle rootlets are easily removed. Kilning also removes the raw flavor (or green-malt flavor) associated with germinating barley, and new aromas, flavors, and colors develop according to the intensity and duration of the kilning process (Craft Beer, 2014).

Maltster. A person who makes or deals in malt (The Free Dictionary, 2014).

pH. Potential of hydrogen; a measure of the acidity or alkalinity of a solution equal to the common logarithm of the reciprocal of the concentration of hydrogen ions in moles per cubic decimeter of solution. Pure water has a pH of seven, acid solutions have a pH less than seven, and alkaline solutions a pH greater than seven (The Free Dictionary, 2014).

Specific gravity. The ratio of the mass of a solid or liquid to the mass of an equal volume of distilled water at 4°C (39°F) or of a gas to an equal volume of air or hydrogen under prescribed conditions of temperature and pressure (The Free Dictionary, 2014).

SRM. Standard Reference Method. A system for analyzing color intensity in beer using a spectrophotometer at a wavelength of 430 nm using a ½ inch cuvette (Chester F. Carlson Center for Imaging Science, 2008).

Type 90 hop pellet. A processed form of leaf hops historically containing 90% of the non-resinous portion of the hop cone (John I. Haas, Inc, 2009).

Wort. Unfermented beer consisting of malt, hops, and any adjuncts before the addition of yeast (Janson, 1996).

Limitations of the Study

The limitations of this study include a small sample size for both the hops and beer used. This was also a bench top study; there was no pilot brewery or commercial brewery available to conduct a long-term large scale dry hop study. No sensory testing was conducted to determine the sensory attributes of the beer with the hop additions.

Chapter II: Literature Review

To provide understanding of the topic of hops and finished beer, the brewing process, the history and chemistry of hops, and dry hopping techniques will be reviewed. The effect pH has on finished beer quality will also be discussed.

The Brewing Process

The process of making beer is a multi-step process that involves malted barley and/or other cereal grains, water, hops, and yeast (Eaton, 2006). Treatment of the barley is described below.

Malting barley is done in three steps: steeping, germination, and kilning. Steeping adds moisture to the barley to promote germination. After steeping, the barley is allowed to germinate in a shallow bed. Germination of the barley produces specific enzymes that start to break down the grain's food reserves. Just before the shoot emerges from the grain the maltster stops the germination by kilning the barley (Eaton, 2006).

The kilning process dries and preserves the malted barley, which gives the characteristic malty flavor (Eaton, 2006). The malted barley is sent to the brewery. The first step is the milling of the malted barley. The malted barley is fractured while passing through a large mill. This makes the grain mass easier to wet and allows for better extraction of carbohydrates during mashing (Eaton, 2006).

After milling, the malted barley is steeped. Hot water is mixed with the milled malted barley and allowed to steep for a set amount of time; this is called mashing. Mashing converts carbohydrates from the malt into fermentable sugars and dextrins due to the enzymes produced during the malting process (Eaton, 2006). Once complete, the malted barley is lautered, the process of separating the wort from the malted barley (Eaton, 2006). The resulting liquid is called wort (Eaton, 2006).

The wort then enters the brew kettle and is brought up to a boil. The hops are added at this point to add bitterness, flavor, and aroma to the final product. After boiling, the hops are removed and the wort is cooled rapidly. Next, the wort is aerated and pumped into a fermentation vessel where the yeast is pitched, a brewer's term for adding the yeast (Eaton, 2006).

During fermentation, the yeast metabolizes the fermentable sugars and produces carbon dioxide, ethanol, flavor, and aroma compounds. After the fermentation is complete the yeast is removed from the beer and the beer ages. Aging will allow for flavor maturation, clarification, and carbonation. The aging process and time varies depending upon the type of beer and brewery. Filteration removes any colloidal matter and yeast. After filtration, the beer is pasteurized for stability and packaged into cans, bottles, kegs, and casks (Eaton, 2006).

Hop History

Beer, or a beverage similar to beer, has been brewed for the last five to six thousand years, but hops have only been used in the brewing process as a regular ingredient since around the 1500's (Daniels, 2000). The hop plant (*Humulus lupulus*) was thought to originate in Asia and is indigenous to the Northern Hemisphere (Roberts & Wilson, 2006). Carl Linne, a Swedish botanist gave hops its scientific name (Hieronymus, 2012). The word *Humulus* comes from *humle*, which is the Swedish word for hops, and *lupulus,* which is the Latin word for hop (Hieronymus, 2012).

In 822 A.D. the Abbot Adalhard of Corbie issued edicts indicating that hops were used during the brewing process (Hieronymus, 2012). Hops used at this time were not cultivated but instead were harvested wild. There is no documentation of when hops were added during the brewing process. Approximately 300 years later, documentation indicated that hops were used during the boiling stage of the brewing process for the preservation effect (Hieronymus, 2012).

Before hops were used for beer production, brewers made a beverage called gruit ale. This was a malt beverage with the addition of herbs and spices such as bog myrtle, rosemary, yarrow, ginger, anise, and sage. It would take centuries before hopped beer would become acceptable (Hieronymus, 2012).

Between the 1500's and 1600's a debate developed in England over the use of hops and regulations were passed to keep gruit ale and hopped beer separate (Steele, 2012). Slowly, hopped beer popularity began to grow, and by 1655 high taxes were placed on hops imported from Europe. Due to importation taxes, farmers started growing hops in 14 counties. In 1710, Parliament banned hop alternatives in the brewing of beer, and by 1800 more than 35,000 acres of hops were planted (Steele, 2012). The ban on hop alternatives along with a tax increase on malt encouraged a greater use of hops in the brewing process. By the 1800's, new beer styles were being established and hopped beers were being referred to as ale (Steele, 2012).

Not long after settlers came to New England, the cultivation of hops began. Settlers in New York soon followed and at that time, 2.5 million pounds of the 3.5 million pounds of hops grown in the United States were from that region (Gorst Valley Hops, 2011). For the next 50 years New York was the leading producer of hops in the United States. Around this time growing shifted to the West Coast of the United States due to the fertile and pest resistant soil (Gorst Valley Hops, 2011). According to the United States Department of Agriculture, in 2012, Idaho, Oregon, and Washington produced a total of 61.2 million pounds of hops on a total of 31,933 acres (United States Department of Agriculture, 2012).

Hop Chemistry

Humulus lupulus is a perennial vine that is dioecious (separate male and female plants). Only the female plant will form the hop cone. The part of the hop cone that the brewer is most concerned about is the lupulin gland. Lupulin glands are small yellow glands that produce the essential oils and resins that are necessary for bitterness, aroma, and flavor in beer (Roberts & Wilson, 2006).

The typical analysis by weight of a dry hop cone shows 8-10% moisture, 40-50% cellulose, up to 15% protein, 8-10% ash, 2% pectin, up to 5% lipids and waxes, 2-5% polyphenols, 0-10% beta acids, 0-22% alpha acids, and 0.5-4% essential oils (Hieronymus, 2012).

Alpha and Beta Acids

Hop resins in the lupulin gland can be divided into two categories: soft resins and hard resins; these can be separated through chemical extraction. The soft resin contains the source of the primary bittering agent in beer, alpha acids, along with beta acids and other uncharacterized substances (Lewis & Young, 2001). The three major alpha acids are humulone, cohumulone, and adhumulone, which are shown in Figure 2. The alpha acids and beta acids each make up about half of the soft resins. The average ratio of the alpha and beta acids is roughly between 0.8 and 1.2 and is hop dependent (Lewis & Young, 2001). There are some European aromatic hops that can be as low as 0.5 and some American varieties as high as 3.0. The American varieties with a ratio as high as 3.0 would be deemed a high alpha acid hop (Lewis & Young, 2001).

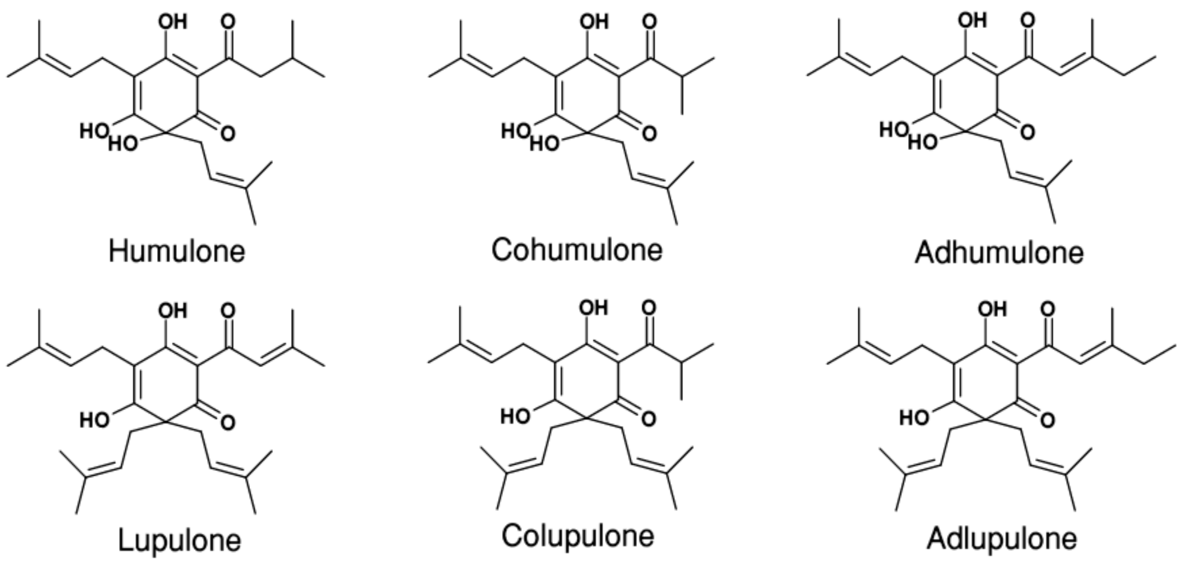


Figure 1. Chemical structure of alpha acids and beta acids (Wild Flower, 2013)

Alpha acids are soluble only to about 3 ppm in water and only trace amounts will be found in finished beer. Beta acids are insoluble in water and there are no trace amounts in finished beer. During the boiling process of beer production the alpha acids will become isomerized due to the heat, becoming iso-alpha acids. Iso-alpha acids are more soluble and are the main component contributing to beer bitterness. The beta acids, however, are unable to isomerize due to the lack of the hydroxy group and there is no chemical reaction that takes place when heated. However, oxidized products from beta acids are water soluble and are found in finished beer; these products are called hulupones. The bittering capability of hulupones is twice as much as the iso-alpha acids (Peacock, 1998).

Essential Oils

The essential oils of hops contribute hop flavor and hop aroma in beer. The oils that provide hop flavor can be put into three categories: hydrocarbon components, oxygen-bearing components, and sulfur components (Fix, 1999).

The hydrocarbon components make up between 50-80% of the total amount of essential oils and involve monoterpenes and sesquiterpenes. The main hydrocarbon structures recognized in beer are myrcene, humulene, caryophyllene, and to a lesser degree, farnesene. See Figure 2 for the chemical structure of the hydrocarbon components. Myrcene is a monoterpene while humulene, caryophyllene, and farnesene are all sesquiterpenes. Out of these hyrdocarbon stuctures, myrcene is the most potent (Briggs, Boulton, Brookes, & Stevens, 2004).

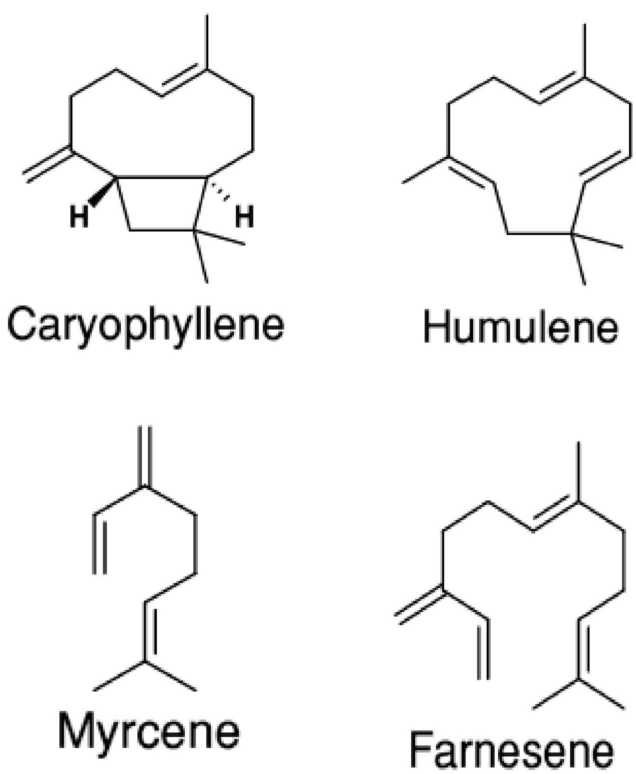


Figure 2. Chemical structure of hydrocarbon components of hop essential oils (The Hop Yard, n.d.)

During the storage of hops, hydrocarbon components oxidize leading to a lower amount of hydrocarbons and an increase of oxygen-bearing components (Briggs, Boulton, Brookes, & Stevens, 2004). The oxidized hydrocarbon components consist of acids, alcohols, esters, and ethers. These components are more likely to survive the boiling process when compared to hydrocarbons, leading to oxidized hydrocarbons in finished beer (Lewis & Young, 2001). This may mean that the oxidized hydrocarbon components of essential oils may be more important for flavor and aroma than actual hydrocarbons. Table 1 (Hieronymus, 2012) shows a variety of chemical compounds and their associated aroma from hop essential oils.

Table 1

Chemical Compounds and Associated Aroma from a Variety of Hop Essential Oils

Chemical Compound	Aroma
Myrcene	Green, resinous
Humulene	Woody, piney
Caryophyllene	Woody
Farnesene	Floral
Citral	Sweet citrus, lemon
Citronellol	Citrusy, fruity
Geraniol	Floral, sweet, rose
Limonene	Citric, orange
Linalool	Floral, orange
Nerol	Rose, citrus

The sulfur compounds in hop essential oils are a very small percentage of the total essential oil content but can be the most aromatic compounds. While still in the field, hop vines are sprayed with elemental sulfur to control mildew. Additionally, mildew is controlled by burning sulfur in the hop kilns. This leads to sulfur-containing compounds labeled episulfides. The level of these compounds are higher when steam distillation occurs at 100^{o} C rather than at 25^{o} C, therefore, more of these compounds will end up in the finished beer when the hops are added late during wort boiling rather than dry hopping (Briggs, Boulton, Brookes, & Stevens, 2004).

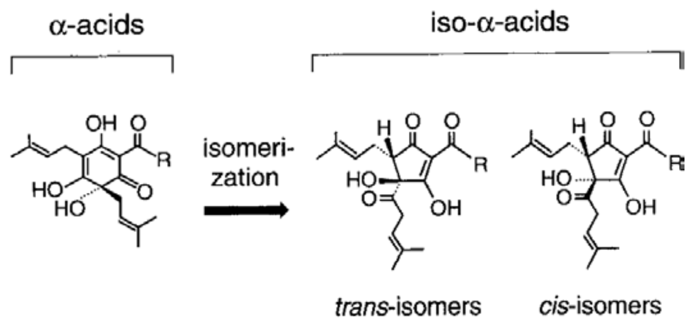
Polysulfide compounds such as dimethyl tetrasulfide and 2, 3, 5-trithiahexane have a cooked vegetable, onion-like, or rubbery, sulfur aroma. These compounds are typically volatized during the boiling process but small amounts of these compounds may find their way into the wort if the hops are added late into the boiling process (Briggs, Boulton, Brookes, & Stevens, 2004).

Polyphenols

Hops contain polyphenols that become extracted and contribute to the physical stability and flavor of beer during the brewing and dry hopping process (Roberts & Wilson, 2006). Between 20% and 30% of polyphenols in wort come from hops. Of those polyphenols, about 80% are condensable compounds and about 20% are hydrolysable compounds (Krottenthaler, 2009). Condensable polyphenols are monomeric polyphenols. Along with their glycosides, condensable polyphenols are able to polymerize to higher molecular products. Polyphenol content in hops are both variety and place of cultivation dependent, with aromatic hops typically having higher amounts of low molecular polyphenols than bittering hops. Low molecular polyphenols are natural antioxidants and increase the reduction power of beer. The low molecular polyphenols protect beer from oxygen, which increases flavor stability. High molecular polyphenols can increase beer color, cause an astringent bitterness to beer flavor, and reduce the colloidal stability. This will also cause beer to become turbid or cloudy. Hop polyphenols will partially be removed during hot and cold trub (protein and protein-tannin complexes) separation, yeast removal, and beer filtration (Krottenthaler, 2009).

Isomerization

The primary hop alpha acids will isomerize during the boiling process and become iso-humulone, iso-cohumulone, and iso-adhumulone (see Figure 3) to visualize the isomerized iso-alpha acids formed). The iso-alpha acids are more soluble in beer and in turn, will lead to the prominent bitterness in beer (Bamforth, 2003).



R = $CH_2CH(CH_3)_2$	humulone	isohumulone
R = $CH(CH_3)_2$	cohumulone	isocohumulone
R = $CH(CH_3)\ CH_2CH_3$	adhumulone	isoadhumulone

Figure 3. Isomerization of alpha acids (Bamforth, 2003)

Factors that encourage faster isomerization are high wort pH, high boil temperature, and hard brewing water. The amounts of dissolved minerals determine water hardness. Factors that encourage iso-alpha acid retention once formed are lower wort gravity, higher wort pH, lower hopping rates, softer brewing liquor, and higher adjunct grains to barley ratio (Roberts & Wilson, 2006).

Dry Hopping Techniques

Dry hopping is a term given to the act of adding hops to the cold side of the brewing process. This includes the fermenter, bright beer tank, and cask. The purpose of adding hops to the cold side of brewing is to extract aromatic and flavorful hop oils into the beer without adding iso-alpha acid bitterness. While this process has been in place since the 18th century, there has been a revitalization of this practice as craft brewers attempt different techniques to get better hop flavor and aroma out of their hops (Hieronymus, 2012).

The traditional way of adding hops to a vessel is to add them from the top. Whether using a large fermenter or cask, the technique would be the same. Brewers today are looking to maximize their hops and have attempted new methods of dry hopping. An example includes making a slurry out of the hops and infusing the slurry into a tank, using a “hop cannon” or a “torpedo” (Hieronymus, 2012).

The hop cannon is a separate pressurized vessel with pellet hops inside. With the use of carbon dioxide, the hops are forced from the hop cannon into the headspace of the tank that contains beer. This allows for less oxygen pick up and the process is more hygienic (Hieronymus, 2012).

The device called a torpedo is a separate vessel packed with whole hops. The torpedo is connected to the bottom of the fermenter and beer will flow from the bottom of the fermenter to the bottom of the torpedo. The beer flows up through the hops and out through the top of the torpedo and back into the fermenter. This allows for constant beer flow through the hops and in turn, extracts the hop oils much more quickly (Hieronymus, 2012).

Although each brewery has a unique way of dry hopping, there does seem to be one understanding. Hops need to be in contact with the beer as long as possible for good extraction of the hop oils. Using a recirculation pump or connecting carbon dioxide to the bottom of the vessel and releasing the gas into the beer to cause settled hops to stay in suspension is a method that results in the hops staying in contact with the beer for as long as possible (Steele, 2012).

Just as techniques of hop entry into the beer vessel are brewer dependent, each brewer has a set temperature, residency time, and hop quantity that is preferred for optimum hop oil extraction. Dry hopping at American craft breweries is happening at a wide range of temperatures, from 11^{o} C to 21^{o} C, with a residency time as short as three days or lasting 14 days or more (Hieronymus, 2012). The amount of hops added varies from 0.5 lbs./bbl. to 3 lbs./bbl. (Wolfe, 2012). There is, however, a limit for each method and hop variety or varieties that are used (Hieronymus, 2012).

pH and the Role it Plays in Finished Beer

Final beer pH has an effect on how beer tastes and how stable the beer is both physically and microbiologically. Typical packaged beer pH is between 4.0 and 4.5; beer with a final pH on either side of this pH range can have negative flavor effects and physical appearance issues. With a pH higher than this range, beer could become contaminated with spoiling microorganisms (Strong, 2011).

Physical Stability

The physical stability of finished beer is critical for consumer acceptance. Beer is typically filtered using various methods to decrease, or ultimately remove, the compounds that increase beer haze. A study conducted by Taylor (1990), shows a direct correlation between beer pH and haze formation and an inverse correlation between beer pH and stability of the foam produced also known as head retention. Taylor proved that at room temperature, beer with a pH between 4.2 and 4.5 had less haze than beer with a pH between 4.6 and 4.8. He also proved that foam retention decreased as the pH value increased. Beer with a pH between 4.2 and 4.5 had better foam stability than beer with a pH between 4.6 and 4.8.

Flavor Effects

When an analysis is conducted on a finished beer the most important aspect is the flavor. Without good, consistent beer flavor all other analysis does not matter. Beer with a pH below

4.2 should be avoided due to acidic beer taste (Esslinger, 2009). Beer with a pH above 4.6 should also be avoided, as it can lead to cloying, the tendency to cling to the tongue, a mouth coating effect, and enhanced chalk/alkaline tones (Fix & Fix, 1997). Taylor (1990) conducted organoleptic and sensory assessments of beer with various pH levels by adjusting the pH using hydrochloric and sulfuric acids or a dilute sodium carbonate solution. He found that beer with a pH below 4.0 tended to be more acidic and drying on the palate with an increase in perceived bitterness. Beer above a pH of 4.0 had an increased mouth feel with an enhanced biscuit, toasted character. Once the beer pH exceeded 4.4 the beer became cloying (sticky) and mouth coating, with a caustic character.

Beer Spoiling Microorganisms

Unlike many other food products, beer is relatively microbiologically stable. Due to the yeast fermentation, a drop in pH, an increase in alcohol, the additions of hop alpha acids, and a lack of nutrients, the finished product inhibits most other microorganisms from growing including the growth of pathogenic organisms. However, despite the factors that help inhibit the growth of unwanted microorganisms, there are a variety of bacteria that can cause beer spoilage (Priest, 2006).

Gram-positive, lactic acid bacteria are the only bacteria that are a major threat to beer. These bacteria do not need oxygen to grow and produce lactic acid as an end product of fermentation. Lactic acid bacteria have become well adapted to acidic environments. These bacteria will grow at pH levels between 3.5 and 6.0 (Priest, 2006).

Lactobacillus brevis is the most common beer spoilage microorganism in breweries (Priest, 2006). Most gram-positive bacteria are sensitive to hop *trans*-Isohumulone and colupulone. These hop components cause leakage of the cytoplasmic membrane and inhibition of amino acid uptake (Priest, 2006). However, *L. brevis* has the *horA* gene; this gene encodes a transporter that expels hop compounds from the cytoplasm, which indicates why *L. brevi* is a major threat to beer and breweries (Priest, 2006).

Pediococcus damnosus is another beer spoilage bacteria that is hop tolerant. This bacterium produces a compound called diacetyl in addition to lactic acid (Priest, 2006). Diacetyl has the characteristic flavor and aroma of butter (Munroe, 2006).

Having good brewing practices along with pasteurization and aseptic packaging techniques will allow for less bacterial contamination in beer. Other factors that play a large role in resistance to bacterial spoilage are high levels of hop compounds, lower free amino nitrogen (FAN) levels, high alcohol content, low oxygen content, high CO_2 content, low levels of carbohydrates in finished beer, and a finished beer pH at the lower end of the 4.0 to 4.5 range (Lewis & Bamforth, 2006).

Chapter III: Methodology

This study examines the effect that dry hopping has on final beer pH. With the popularity of craft beer at an all-time high, craft breweries are setting out to separate themselves from other innovative craft breweries. One way to accomplish this is to add hops to the fermentation process or the post fermentation process, which allows for a large extraction of hop flavor and aroma into the beer without adding the signature hop bitterness. This study was conducted to determine if adding hops during the post-fermentation phase changes the final pH of the beer. This chapter includes the subject selection, instrumentation, sample preparation, determination of hop and beer sample attributes, and data analysis.

Sample Selection and Description

For this experiment, six hop varieties and four beer varieties were used to determine if dry hopping has an effect on the final pH of beer. The hops used were a type 90 pellet hop and varieties were chosen based solely on their alpha acid content. The six hop varieties can be put into three categories: low, medium, and high alpha acid. Polish Lublin (4.2% alpha acids) and Willamette (5.0% alpha acids) are low alpha acid hops, Styrian Aurora (8.1% alpha acids) and Northern Brewer (8.5% alpha acids) are medium alpha acid hops, while Centennial (12.0% alpha acids) and Columbus (15.3% alpha acids) are high alpha acid hops.

The four beer varieties were chosen based on visual appearance in terms of color. The color variation was due to the different malts used in the brewing process. Each commercial beer was also given a code, Commercial Beer A (CBA), Commercial Beer B (CBB), Commercial Beer C (CBC), and Commercial Beer D (CBD). The color of beer chosen was blonde, amber, red, and black.

Sample Preparation

The six hop varieties that were used in the study were vacuum-sealed and stored in a freezer when not being analyzed. When needed, the hops were taken out of the freezer, the bags were opened and approximately five grams of each hop variety were removed. The hops being used were then ground in a blender to create a homogenous sample and for ease of weighing.

Figure 4. Hop sample after grinding (photograph by M. Schmick)

For each beer variety the beer was degassed to stabilize the pH. This was conducted by adding beer to a beaker and mixing the beer on a stir plate for 15 minutes.

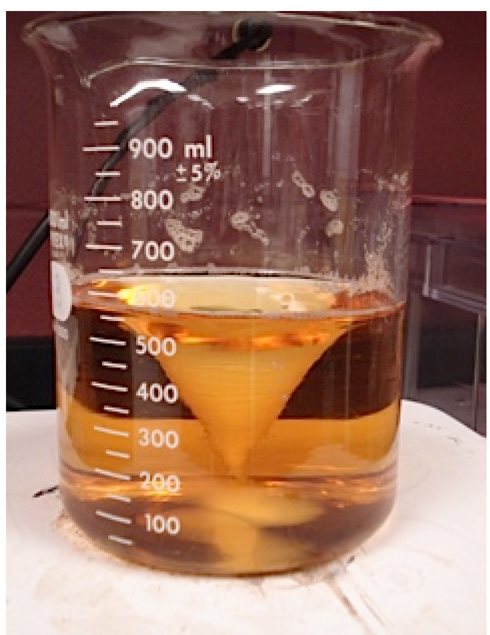


Figure 5. Beer being degassed for preparation for dry hopping (photograph by M. Schmick)

pH Analysis of Beer

A calibrated pH meter was used to determine the pH of beer with carbonation and without carbonation. Room temperature beer was slowly poured into a beaker to prevent degassing from occurring. The pH probe was inserted into the beer and the pH value was recorded once the pH meter (Fisher Scientific Accumet Basic AB15 Plus) stabilized. The same sample was then degassed and the pH was recorded. This value was the pH value of the beer before dry hopping. Each beer sample was analyzed in triplicate.

Determination of Beer Color

Beer color was determined using American Society of Brewing Chemists method Beer-10, A (American Society of Brewing Chemists, 1992) using a Varian Cary UV/Visible Spectrophotometer. The wavelength was set for 430 nm and distilled water was used as a blank sample. Each beer variety was run in triplicate. The following equations were used to determine beer color (European Brewery Convention).

$$(A_{1/2}, 430\text{ nm}) = 1.27 \times \text{ABS}$$

$$\text{Beer Color (Standard Reference Method)} = 10 \times (A1/2, 430\text{ nm})$$

$$\text{Beer Color (European Brewery Convention)} = 1.97 \text{ X SRM}$$

Determination of Final Beer Specific Gravity

Final beer specific gravity was determined with the use of a hydrometer. Degassed beer was poured into a hydrometer tube and the hydrometer was placed into the beer. The density of the beer was recorded and conducted in triplicate at 15.5^{o} C.

Total Beer Acidity Analysis

Total beer acidity was determined using ASBC method Beer 8 A (American Society of Brewing Chemists, 1992). Exactly 50 ml of degassed beer was placed into a titration flask and the pH was analyzed. While continually stirring the beer sample 0.1*N* NaOH was added until the beer pH reached 8.2. The amount of 0.1*N* NaOH was recorded and each titration was conducted in triplicate. The following equation was used to determine total acidity as "lactic acid".

$$\text{Total Acidity} = \frac{\text{ml } 0.1\text{N NaOH x } 0.9}{\text{ml beer x specific gravity of beer}}$$

pH Analysis of Hops

To determine the pH of each hop variety, 2.5 g of homogenous ground hops were blended with 15 ml of distilled water. After the slurry was prepared, the pH probe was inserted into the slurry and once stabilized, the pH was recorded. This was done in triplicate for each hop variety.

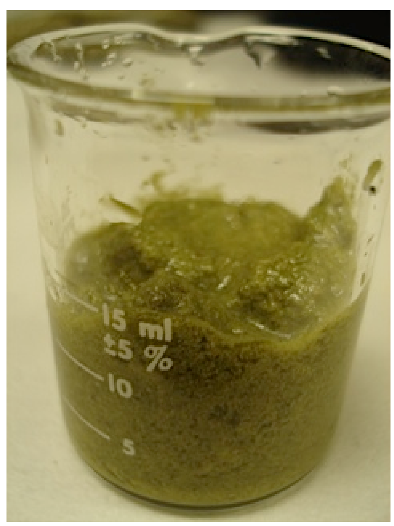


Figure 6. Hop slurry for pH analysis (photograph by M. Schmick)

Ash Analysis of Hops

Three grams of ground homogenous hop sample was placed into a crucible and set inside a furnace. The furnace temperature was set to 575^{o} C for 24 hours. After the 24-hour time period, the samples were placed in a desiccator for cooling purposes. Once the samples were cooled they were re-weighed. The weight of the ash was divided by the initial weight of the hop samples to determine the percentage of ash. Ash analysis was conducted in triplicate. The following equation shows how ash percentage was determined.

$$\% \text{ ash (dry basis)} = \frac{\text{(weight after ashing - tare weight of crucible)}}{\text{(initial weight of sample)}} \times 100$$

Water Activity Analysis

Two grams of ground homogenous hop sample was placed into an Aqua Lab 3TE water activity meter to determine the water activity level. Water activity was conducted in triplicate.

Bench Top Dry Hopping

To determine the effect dry hops have on finished beer pH, bench top dry hopping was conducted using four different commercial beer samples and six varieties of hops. A 100 ml aliquot of degassed beer at room temperature ($20^{o}C$ – $22^{o}C$) was placed into 600 ml beakers; the initial beer pH was analyzed at this time. The addition of 0.194 g (0.5 lbs./bbl.) of ground homogenous hop sample was added to each beaker and mixed for five minutes on a VWR DS-500 Orbital Shaker at 125 RPM. After mixing, the pH was analyzed to determine the effect dry hops had on beer pH. This process continued until an equivalent of 3.0 lbs./bbl. was achieved and was conducted in triplicate.

Figure 7. Dry hops mixing on an orbital shaker (photograph by M. Schmick)

Data Analysis

Microsoft Excel was used to determine mean and standard deviation of all samples analyzed. Single factor ANOVA, Tukey's HSD, and Pearson's correlation was conducted using SPSS (IBM SPSS Statistics 20). All analysis conducted were evaluated at a significanct difference of $p<0.05$.

Chapter IV: Results and Discussion

The purpose of this study was to determine if the act of dry hopping would influence the final pH. Six hop varieties and four beer varieties were used in this study. Hop and beer chemistry analysis was conducted on each hop and beer sample. Data collected for hop chemistry analysis included pH, % ash, and water activity. The alpha acid content of each hop sample was determined by the hop manufacturer. Data collected for beer chemistry analysis included color, pH with CO_2, pH without CO_2, total beer acidity, and specific gravity. The pH was analyzed during bench top dry hopping trials.

Beer Analysis

Beer chemistry analysis was conducted for color, pH with CO2, pH without CO2, total beer acidity after CO_2 was removed, and specific gravity. Results can be seen in Table 2.

Table 2

Chemistry Analysis of Four Commercially Available Beers

Chemistry Analysis	CBA	CBB	CBC	CBD
Color (EBC)	7.8	21.2	41.8	153.8
pH With CO_2	4.20	4.26	4.10	4.27
pH Without CO_2	4.33	4.31	4.22	4.33
Total Acidity	0.15%	0.17%	0.16%	0.17%
Specific Gravity	1.012	1.015	1.016	1.019

CBA= Commercial Beer A, CBB= Commercial Beer B, CBC= Commercial Beer C, CBD= Commercial Beer D
Color Method used was based on European Brewery Convention (EBC)

Beer Color

The method used for color analysis was based on the European Brewery Convention (EBC) method. The mean color of the four commercial beer samples are as follows: CBA = 7.8, CBB = 21.2, CBC = 41.8 and CBD = 153.8. Lower numbers indicate a lighter beer color. In Figure 8 the beers left to right are: CBA, CBB, CBC, CBD. Beer color varies due to the types of malt and grains used in the brewing process.

Figure 8. Color of beer samples (photograph by M. Schmick)

Beer Acidity

Mean beer acidity was similar in all four commercial beer samples (CBA = 0.15%, CBB = 0.17%, CBC = 0.16% and CBD = 0.17%). Acidity in beer is produced during the fermentation process; yeast produce organic acids that reduce the beer pH and increase beer acidity (Esslinger, 2009). Dark malts are more acidic than lighter colored malts and adjuncts (De Clerck, 1957); this could explain why CBA is slightly lower in acidity than the other samples. Even though CBB is lighter than CBC and CBD it has a higher acidity than CBC and has the same acidity as CBD. Because each of these beers was produced at a different brewery, the exact brewing process may differ causing the color of the beer and the acidity levels to not correlate.

Specific Gravity

The mean specific gravity of the four commercial beers were as follows: CBA = 1.012, CBB = 1.015, CBC = 1.016, and CBD = 1.019. The final gravity of a beer is determined by the carbohydrate composition of the beer. During the mashing process, alpha and beta amylase enzymes break down complex carbohydrates from the malt to produce simple carbohydrates that are easily fermented by brewer's yeast (Palmer, 2006). These carbohydrates include: glucose, fructose, sucrose, maltose, and maltotriose. The determining factor for the percentage of each is the temperature of the mash and how long the mash is at the set temperature (Palmer, 2006). A brewer may want a beer with less residual carbohydrates so the mash temperature will be lower; this will be more favorable for beta-amylase. A brewer that wants to keep more complex sugars in the beer will prefer a higher mash temperature that will favor alpha-amylase enzymes (Palmer, 2006). Using a hydrometer will only give the specific gravity of the beer; other lab equipment such as a HPLC may be used to identify the actual carbohydrate spectrum.

Beer pH

All four commercial beer samples were analyzed for mean pH with CO_2 in solution and out of solution. With CO_2 in solution, the mean pH was CBA = pH 4.20, CBB = pH 4.26, CBC = pH 4.10, and CBD = pH 4.27. After being degassed, the same samples were then checked for pH and the following mean pH was recorded: CBA = pH 4.33, CBB = pH 4.31, CBC = pH 4.22, and CBD = pH 4.33. All of the commercial beer samples were similar in final beer pH except CBC. This beer sample was 0.09 lower in pH than CBB and 0.11 lower in pH than CBA and CBD. This may be due to the treatment of the brewing water and/or the fermentation practices of that brewery.

Hop Chemistry

Hop chemistry analysis was conducted for pH, % ash, and water activity (Aw); the % alpha acid (%AA) analysis was already determined by the hop processor. Results are seen in Table 3. The Columbus and Centennial varieties had the highest alpha acid content.

Table 3

Chemistry Analysis of Six Hop Varieties

Chemistry Analysis	Polish Lublin	Willamette	Styrian Aurora	Northern Brewer	Centennial	Columbus
pH	5.28	5.33	5.28	5.06	5.32	5.19
% Ash	7.49	8.85	7.79	9.05	8.46	8.63
Aw	0.55	0.527	0.540	0.518	0.555	0.495
% AA	4.20	5.00	8.10	8.50	12.00	15.30

Aw = Water Activity, % AA = % Alpha Acid

Water Activity of Hops

During hop processing, hops are picked off of the bine and kilned. This reduces the moisture content of the hops for shelf-stability. Water activity, although not the same as moisture content, can provide information about how dry a product is by the amount of binding water in the product. The mean water activity of the six hop varieties were as follows: Polish Lublin = 0.550, Willamette = 0.527, Styrian Aurora = 0.540, Northern Brewer = 0.518, Centennial = 0.555, and Columbus = 0.495. The Northern Brewer and the Columbus hop varieties demonstrated the lowest water activity.

pH of Hops

Due to the low moisture of the dried process hop pellets, analyzing the pH was difficult for obtaining an accurate reading. The addition of 15 ml of distilled water to 2.5 g of hop pellet was the only way to develop a slurry with an acceptable consistency to acquire a pH reading. The hop pellets absorbed a large majority of the distilled water, therefore, adding six times as much distilled water as hop pellets by weight was used. The mean pH of the hop samples Polish Lublin = pH 5.28, Willamette = pH 5.33, Styrian Aurora = pH 5.28, and Centennial = pH 5.32

were all similar with the exception of Columbus (pH = 5.19) and Northern Brewer (pH = 5.06). Due to the amount of distilled water added, the mean pH of the hop samples may not be accurate. However, one could argue that this test shows there is a difference in hop pH depending on the variety of hop. In this incidence, Northern Brewer and Columbus hop varieties demonstrated the lowest pH.

Percent Ash of Hops

The mean ash content of the six hop varieties had a range between 7.49% (Polish Lublin) to as high as 9.05% (Northern Brewer). Styrian Aurora had a mean ash percentage of 7.79% while Centennial, Columbus, and Willamette had a mean ash percentage of 8.46%, 8.63%, and 8.85%, respectively. Centennial, Northern Brewer, and Willamette varieties were found to have the most percent ash. The data established from the ash analysis corresponds similarly with the ash content of 8-10% previously reported by Hieronymus (2012) for hop varieties.

pH Values per Hop Dose

Dry hopping rates equivalent to 0.5 lbs./bbl. were used for this study. Hops were dosed at this rate every five minutes. After each five minute mixing interval the pH was recorded. The mean pH values of the four commercial beer samples after being dry hopped can be seen in figures 9, 10, 11, and 12.

Figure 9 shows that when CBA was dry hopped there was an increase in beer pH. Average pH increase per dosing rate equivalent to 0.5 lbs./bbl. are as follows: Polish Lublin = pH 0.048, Willamette = pH 0.055, Styrian Aurora = 0.062, Northern Brewer = pH 0.043, Centennial = pH 0.050, and Columbus = pH 0.054.

Styrian Aurora produced the largest total increase in pH with a total mean pH reading of 4.693, which is a total pH increase of 0.363. Northern Brewer produced the smallest increase with a mean pH reading of 4.587 with a total pH increase of 0.257. As the hop dosing rates increased there was a greater distribution of pH values. At a hop dosing rate equivalent to 2.5 lbs./bbl., the pH values remained within 0.1 of each other. The largest gap came at the 3.0 lbs./bbl. equivalent hop-dosing rate, which resulted in a pH difference of 0.116.

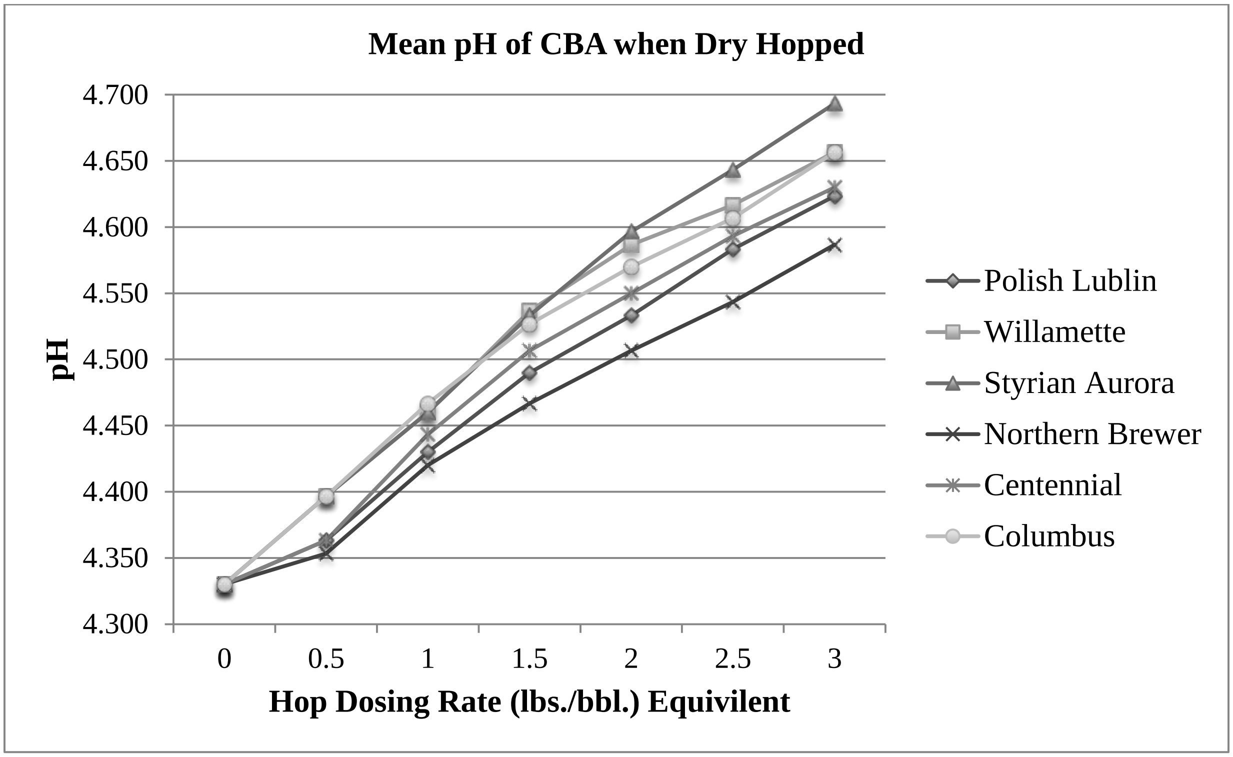


Figure 9. Mean pH values for Commercial Beer A (CBA) after dry hopped

Figure 10 shows that when CBB was dry hopped there was an increase in beer pH. Average pH increase per dosing rate equivalent to 0.5 lbs./bbl. are as follows: Polish Lublin = pH 0.043, Willamette = pH 0.049, Styrian Aurora = 0.056, Northern Brewer = pH 0.037, Centennial = pH 0.046, and Columbus = pH 0.048.

Styrian Aurora produced the largest total increase in pH with a total mean pH reading of 4.643, which is a total pH increase of 0.333. Northern Brewer produced the smallest increase with a mean pH reading of 4.533, which is a total pH increase of 0.223. As the hop dosing rates increased there was a greater distribution of pH values. At a hop dosing rate equivalent to 2.5

lbs./bbl. the pH values remained within 0.09 of each other. The largest gap occurred at the 3.0 lbs./bbl. equivalent hop-dosing rate, resulting in a pH difference of 0.11.

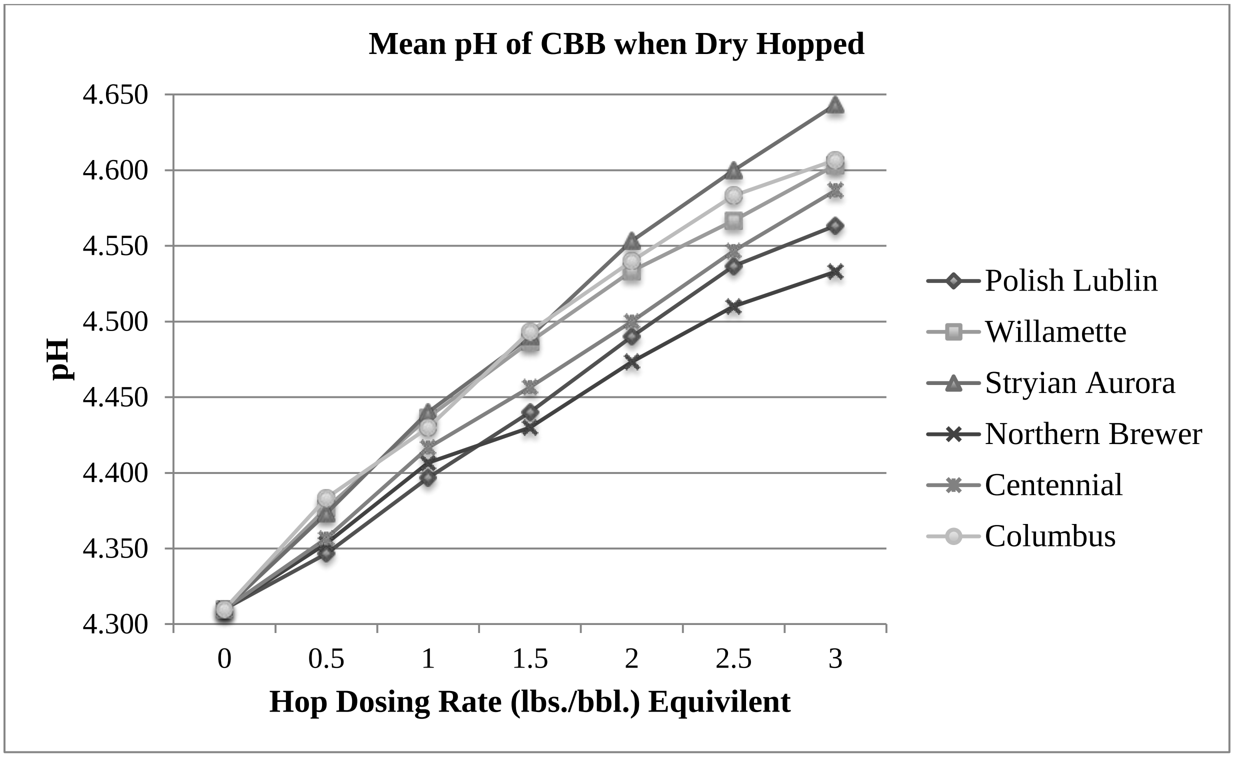


Figure 10. Mean pH values for Commercial Beer B (CBB) after dry hopped

Figure 11 shows that when CBC was dry hopped there was an increase in beer pH. Average pH increase per dosing rate equivalent to 0.5 lbs./bbl. are as follows: Polish Lublin = pH 0.045, Willamette = pH 0.051, Styrian Aurora = 0.059, Northern Brewer = pH 0.041, Centennial = pH 0.050, and Columbus = pH 0.051.

Styrian Aurora produced the largest total increase in pH with a total mean pH reading of 4.563, which is a total pH increase of 0.343. Northern Brewer produced the smallest increase with a mean pH reading of 4.463, which is a total pH increase of 0.233. At a hop dosing rate equivalent to 2.5 lbs./bbl. the pH values remained within 0.090 of each other. The largest gap came at the 3.0 lbs./bbl. equivalent hop dosing rate, which resulted in a pH difference of 0.110.

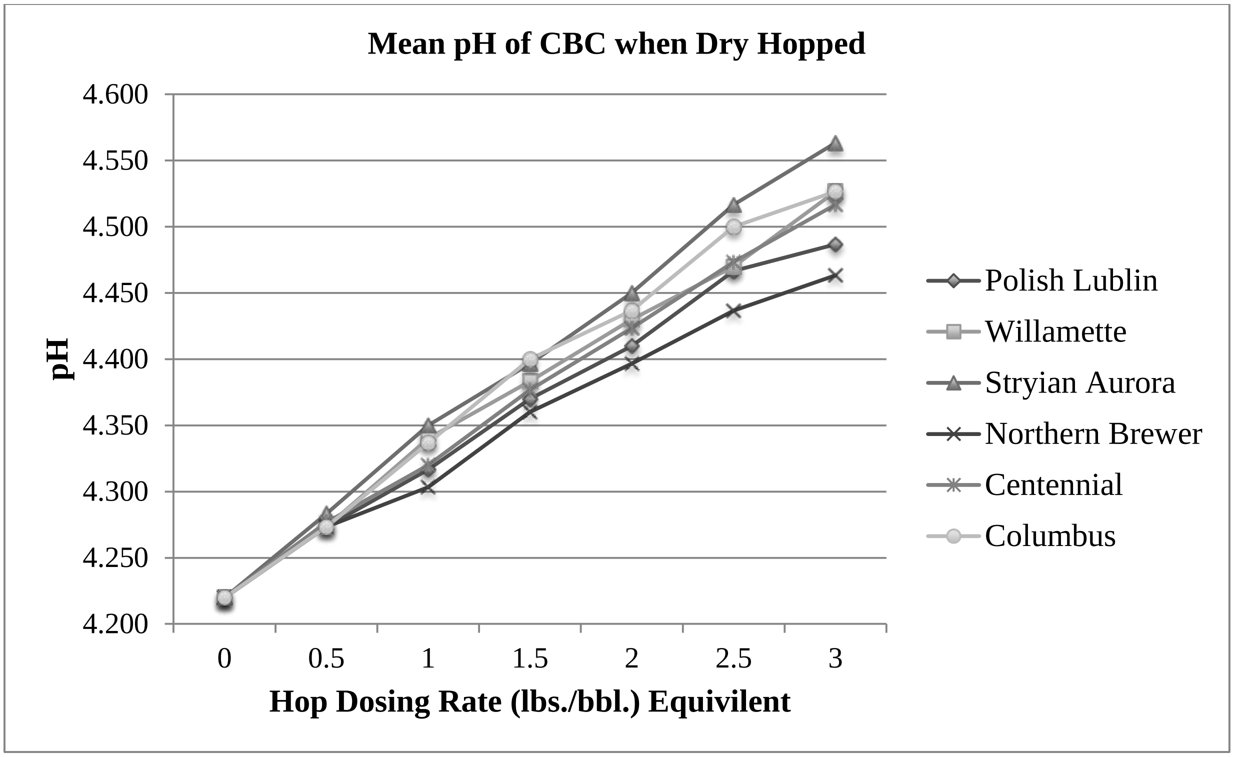


Figure 11. Mean pH values for Commercial Beer C (CBC) after dry hopped

Figure 12 shows that when CBD was dry hopped there was an increase in beer pH. Average pH increase per dosing rate equivalent to 0.5 lbs./bbl. are as follows: Polish Lublin = pH 0.040, Willamette = pH 0.043, Styrian Aurora = 0.048, Northern Brewer = pH 0.037, Centennial = pH 0.042, and Columbus = pH 0.045.

Styrian Aurora produced the largest total increase in pH with a total mean pH reading of 4.620, which is a total pH increase of 0.29. Northern Brewer produced the smallest increase with a mean pH reading of 4.537, which is a total pH increase of 0.207. At a hop dosing rate equivalent to 2.5 lbs./bbl. the pH values remained within 0.086 of each other. This was slightly higher than the 3.0 lbs./bbl. equivalent hop dosing rate, which resulted in a pH difference of 0.083.

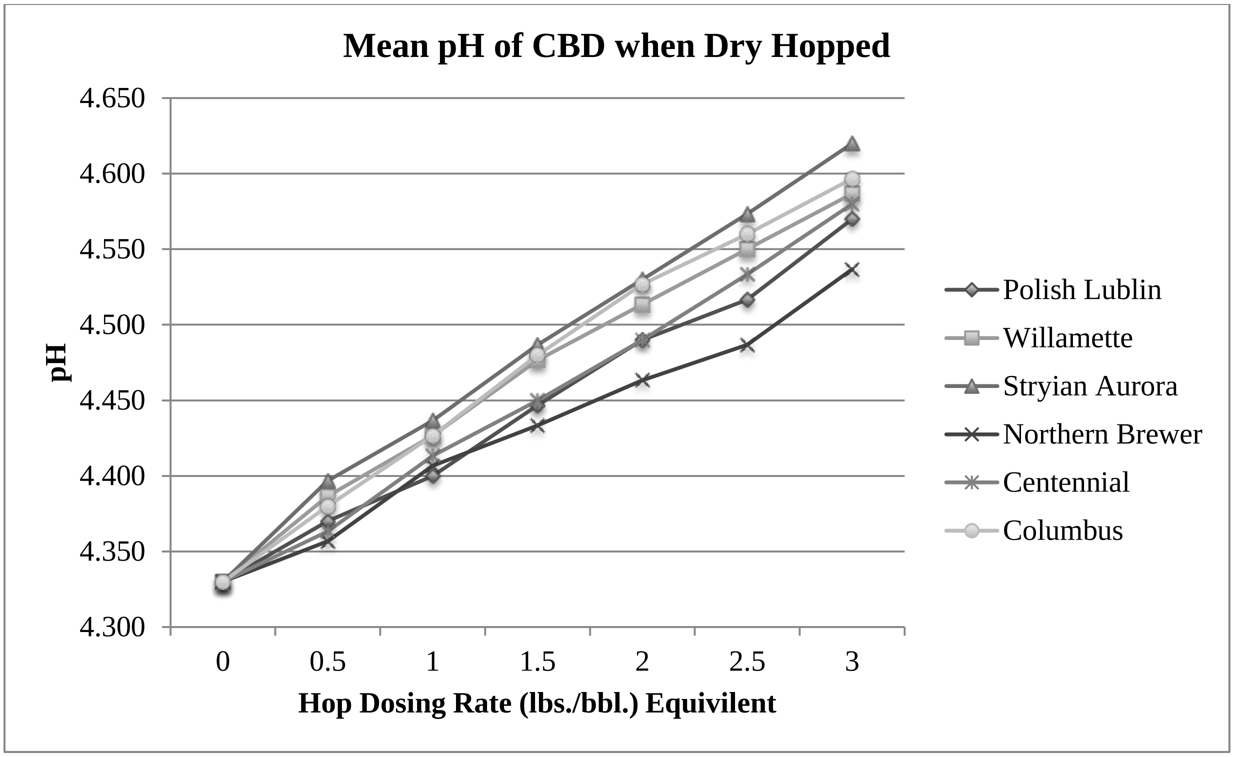


Figure 12. Mean pH values for Commercial Beer D (CBD) after dry hopped

All six hop varieties chosen for this study increased the pH of each beer sample. The six hop varieties did not increase the beer pH at the same rate. These findings coincide with a study conducted by Kaltner et al. (2013).

Kaltner et al. (2013) discovered that dry hopping slightly effects beer pH over time. Data from that study indicates that depending on the beer variety, hop variety, and hop contact time, the pH may raise up 0.2. Other data from the Kaltner et al. (2013) study showed that the pH might not rise at all. Kaltner et al. (2013) used a hop dosing rate of 85g/hl, which is the equivalent to 0.2194 lbs./bbl, which is much less than the hop dosing rate used for the current study.

Dry Hop Analysis

Data collected throughout this study has proven that the act of dry hopping beer has an impact on the final beer pH. Adding hops in the equivalent of 0.5 lbs./bbl. led to a rise between

0.040 and 0.056 of mean pH depending on the hop variety. Single factor ANOVA was conducted on both the four commercial beer samples and the six hop varieties. Based on the results of this study, there is not a significant difference ($p<0.05$) in pH increase between the four commercial beer samples. However, there is a significant difference ($p<0.05$) between the six hop varieties when a hop dose rate equivalent to 0.5 lbs./bbl. of hops are added. Table 4 shows the mean increase, standard deviation, and significance of the analyses conducted.

Table 4

Mean pH Increase of Four Commercial Beers from Six Hop Varieties at an Equivalent Dry Hop Dose Rate of 0.5 lb./bbl.

Hop Variety	pH Increase of Beer (Mean ± SD)
Polish Lublin	0.044 ± 0.003^{bc}
Willamette	0.050 ± 0.005^{ab}
Styrian Aurora	0.056 ± 0.006^{a}
Northern Brewer	0.040 ± 0.003^{c}
Columbus	0.047 ± 0.004^{abc}
Centennial	0.050 ± 0.004^{ab}

* The means with different superscripts indicate a significant difference ($p<0.05$) by Tukey's HSD

Table 4 shows the mean pH increase of the six hop varieties in all four commercial beers. Styrian Aurora produced the largest mean pH increase per equivalent dry hop dose rate of 0.5 lb./bbl. but was not significantly different from Willamette, Columbus, or Centennial; the pH increase of Styrian Aurora had a significantly higher increase than Polish Lublin and Northern Brewer. Northern Brewer produced the lowest pH increase that was not significantly different from Columbus or Polish Lublin. This means that Northern Brewer and Polish Lublin were similar in producing smaller pH increases.

Single factor ANOVA was conducted on both the four commercial beer samples and the six hop varieties for the hop dose rate equivalent to 3.0 lbs./bbl. It was determined that there was a significant difference ($p<0.05$) in pH increase between the four commercial beer samples and a significant difference ($p<0.05$) between the six hop varieties. Table 5 shows the mean pH increase and standard deviation of the analysis conducted.

Table 5

Mean pH Increase of Four Commercial Beers from Six Hop Varieties at an Equivalent Dry Hop Dose Rate of 3.0 lb./bbl.

Hop Variety	pH Increase (Mean ± SD)
Polish Lublin	0.263 ± 0.023[bc]
Willamette	0.296 ± 0.030[ab]
Styrian Aurora	0.332 ± 0.031[a]
Northern Brewer	0.233 ± 0.022[c]
Columbus	0.281 ± 0.023[abc]
Centennial	0.300 ± 0.025[ab]

* The means with different superscripts indicate a significant difference ($p<0.05$) by Tukey's HSD

Table 5 shows the mean pH increase of the six hop varieties in all four commercial beers. Styrian Aurora produced the largest mean pH increase per equivalent dry hop dose rate of 3.0 lbs./bbl. Styrian Aurora increased beer pH significantly greater than Polish Lublin or Northern Brewer. Willamette and Centennial increased beer pH significantly greater than Northern

Brewer. Northern Brewer increased beer pH significantly less than all hop varieties except Polish Lublin.

Table 6 shows the mean pH increase of the four commercial beers at a hop dose rate of 3.0 lbs./bbl. CBA had the greatest mean pH increase at a dry hop dose rate equivalent of 3.0 lbs./bbl. with a pH increase of 0.311, which was significantly higher compared to CBD. However, both CBB and CBC were not significantly different from CBA or CBD. CBD's pH increase was the lowest at a pH increase of 0.252. Compared to CBA this was a difference of pH 0.059.

Table 6

Mean pH Increase of Four Commercial Beers at an Equivalent Dry Hop Dose Rate of 3.0 lbs./bbl.

Beer	pH Increase (Mean ± SD)
CBA	0.311 ± 0.036^{a}
CBB	0.280 ± 0.038^{ab}
CBC	0.294 ± 0.035^{ab}
CBD	0.252 ± 0.028^{b}

CBA= Commercial Beer A, CBB= Commercial Beer B, CBC= Commercial Beer C, CBD= Commercial Beer D

* The means with different superscripts indicate a significant difference ($p<0.05$) by Tukey's HSD

It was determined that each beer variety and hop variety impacted the change in pH differently. Similar results were found in the Kaltner et al. study (2013). In Kaltner et al.'s study, each hop variety increased the pH between 0.0 and 0.2 at a hop dosing rate equivalent of 0.2194 lbs./bbl. Some of the hop varieties increased the pH of beer differently depending on the beer style. A hop variety called Mittelfruh raised a lager beer a pH of 0.1 in a two week dry hopping trial while a two week dry hopping trial with a wheat beer showed an increase in pH of 0.2 (Kaltner et al., 2013).

Correlation Between Hop Chemistry Analysis and pH Increase

Pearson's correlation was utilized to determine if there was a significant correlation ($p<0.05$) between the ash content, water activity, pH, and alpha acid content of the six hop varieties and the mean increase in beer pH for the four commercial beer samples. After the analysis was conducted it was determined that the ash content of the hops ($p=0.405$), water activity ($p=0.809$), pH ($p=0.116$), and alpha acid content ($p=0.509$) did not have any correlation with the increase in beer pH from dry hopping.

Correlation Between Beer Chemistry Analysis and pH Increase

Pearson's correlation was utilized to determine if there was a significant correlation ($p<0.05$) between the beer color, initial pH without CO_2, total beer acidity, specific gravity, and mean increase in beer pH for the four commercial beer samples. It was determined that the beer color ($p=0.111$), pH without CO_2 ($p=0.749$), total beer acidity ($p=0.983$), and specific gravity ($p=0.077$) did not have any correlation with the increase in beer pH from dry hopping.

This study employed four commercially available beer samples. Beer color, total beer acidity, specific gravity, and beer pH was analyzed in triplicate. Six varieties of dry hops were employed for this study and analyzed for pH, ash content, water activity, and alpha acid content. All six hop varieties were added to each of the four beers and were analyzed in triplicate for any change in pH of the beer samples. All analyses were reported in the results section. The significance of these findings, limitations, and conclusions are provided in Chapter 5.

Chapter V: Conclusion

The objective of this study was to determine the effect that dry hopping has on the final pH of beer. Four commercially available beer samples were utilized in this study and were analyzed for color, pH, total acidity, and specific gravity. Six commercially available hop samples were utilized for this study and were analyzed for ash content, pH, and water activity. The alpha acids content of the six hop samples were predetermined by the hop pellet processor. These sample attributes were used to determine if there was a correlation between the individual attributes and the change in beer pH. This chapter will discuss the limitations, conclusions, and recommendations for further studies.

This study is an important step into discovering why the pH rises during the dry hopping process. Each hop variety produced different results during this trial and each beer variety had a different rate of pH increase. More research is needed to definitively answer why the pH rises with the addition of hops and why each hop raises the pH differently. Likewise, more research must be conducted to determine what attribute in beer allows for a different rise in beer pH during dry hopping.

Data shows that dry hopping increased finished beer pH. At a dry hop dosing rate equivalent of 3.0 lbs./bbl., Styrian Aurora had the largest impact on beer pH with a mean pH increase of 0.332 ± 0.031. This impact was not significantly different than Centennial with the next highest increase of 0.300, Willamette with 0.296, or Columbus at 0.281 but was significantly higher than the Polish Lublin and Northern Brewer. Northern Brewer had the lowest increase in beer pH with a mean pH increase of 0.233 ± 0.022, but this was not significantly different from Polish Lublin (0.263) or Columbus (0.281). This could be interpreted that the Northern Brewer and Polish Lublin would increase beer pH the least if added in the dry hopping process.

Data analysis shows that there is no significant difference ($p<0.05$) for beer styles used in the study at a hop dose rate equivalent of 0.5 lbs./bbl., however, at a dry hop dosing rate equivalent of 3.0 lbs./bbl. there is a significant difference ($p<0.05$). The pH increase was largest for CBA with a mean pH increase of 0.311 ± 0.036, followed by CBC, CBB, and lastly CBD with a mean pH increase of 0.252 ± 0.028. The dark beer pH increase was significantly lower than the blonde beer, but not significantly different from the amber or red beer with this addition. It could be concluded that if this level of hop addition is necessary to obtain the necessary flavor, then the addition could be achieved more successfully without large pH increases in the darker beers.

In this study there were no significant correlations ($p<0.05$) found between the hop attributes analyzed and mean pH increase from dry hopping. The beer attributes analyzed showed no significant correlation ($p<0.05$) in regard to beer pH increase from dry hopping.

The results of this study have indicated that dry hopping will effect the overall pH of beer, but to what effect is still unknown. More trials are needed to determine what contact time, temperature of the beer, dry hopping techniques, and other hop and beer attributes have in regard to the pH increase during dry hopping. One can assume that an increase in pH, flavor defects, microbial stability, and physical stability may be compromised if the pH rises too much during the dry hopping process.

Limitations

There were limitations to this study, the first being the sample number of both hops and beers. There are almost 100 commercially available hop varieties on the market and more are developed each year. With the use of only six varieties, the relationship between hop attributes and pH increase was not sufficiently analyzed. The same dilemma happened when only testing four beer samples, as there are nearly 100 beer styles and thousands of beer brands on the market. The second limitation encountered during this research was that this was conducted as a bench top study. A large scale facility that has the ability to dry hop beer for an extended period of time, dry hop beers multiple ways, and utilize different dry hopping temperatures would be essential in determining the impact that dry hopping has on beer pH on a commercial scale. The third limitation was the lack of other studies to gather information from. This field of study lacks research and the data necessary for valid comparisons.

Recommendations

With a lack of data to conclude the reason for a rise in pH during dry hopping, further studies must be completed. The following recommendations will assist in fully understanding the significance of pH rise during dry hopping and its effect on the final product.

1) In this study a single time and temperature was established for dry hopping. Dry hopping at different temperatures (5^oC, 10^oC, 15^oC) and various times (12 hours, 24 hours, 72 hours) while still using the current hopping rates of 0.5 lbs./bbl. – 3.0 lbs./bbl. is recommended. This would allow for a greater understanding into the environmental factors that may contribute to the rise in final beer pH.
2) Further analysis should be completed on each hop variety to determine the exact compounds that may contribute to the pH increase when dry hopping.
3) Further analysis should be conducted on each beer variety to determine the exact attribute that may cause a buffering impact on pH rise when dry hopped.

4) Further analysis should be conducted to determine why there is a negative correlation between final specific gravity and the increase of beer pH during dry hopping.
5) A commercial scale of this project should be completed to determine if the same rise in pH happens in a large fermenter in the same way as demonstrated in the bench top study.
6) Sensory analysis should be completed to determine if the rise in pH affects the flavor of the finished beer. Food grade acids such as phosphoric or lactic should be dosed into the final dry hopped beer to lower the pH to determine if the lower pH of the final beer has better flavor and drinkability than the control.
7) Clarity and foam analysis should be conducted to determine if a beer that has been dry hopped and has a high pH still produces the same clarity and foam quality as the same beer but with a lower pH.
8) Microbiological tests should be conducted to determine if a dry hopped beer with a high pH is as stable as a dry hopped beer at a low pH.

References

American Society of Brewing Chemists. (1992). Beer method 10 A. *ASBC methods of analysis* (8th ed.; pp.1-2). St. Paul, MN: American Society of Brewing Chemists.

American Society of Brewing Chemists. (1992). Beer method 8 A. *ASBC method of analysis* (8th ed.; pp. 1-2). St. Paul, MN: American Society of Brewing Chemists.

Bamforth, C. (2003). *Beer: Tap into the art and science of brewing* (2nd ed.). New York: Oxford Univeristy Press, Inc.

Baxter, E. D., & Hughes, P. S. (2001). *Beer: Quality, safety and nutrional aspects.* Cambridge: The Royal Society of Chemistry.

Brewers Association. (2013, July). *Brewers association reports continued growth for U. S. craft brewers*. Retrieved November 5, 2013, from www.brewersassociation.org/pages/media/press-release/show?title+brewers-association-reports-continued-growth-for-u-s-craft-brewers

Briggs, D. E., Boulton, C. A., Brookes, P. A., & Stevens, R. (2004). *Brewing science and practice.* Boca Raton, FL: CRC Press.

Chester F. Carlson Center for Imaging Science. (2008). *Beer color*. Retrieved from http://www.cis.rit.edu/fairchild/PDFs/BeerColorHandout.pdf

Craft Beer. (2014). *Beer glossary*. Retrieved from http://www.craftbeer.com/beer-studies/beer-glossary

Daniels, R. (2000). *Designing great beers: The ultimate guide to brewing classic beer styles.* Boulder, CO: Brewers Publications.

De Clerck, J. (1957). *The text book of brewing* (Vol. I). London: Chapman and Hall Ltd.

Eaton, B. (2006). An overview of brewing. In F. G. Priest, & G. G. Stewart (Eds.), *Handbook of brewing* (2nd ed., pp. 77-87). Boca Raton, FL: CRC Press.

Esslinger, H. M. (2009). Fermentation, maturation, and storage. In H. M. Esslinger (Ed.), *Handbook of brewing: Processes, technology, markets* (pp. 209- 212). Weinheim, Germany: Wiley-VCH.

Fix, G. J., & Fix, L. A. (1997). *An analysis of brewing techniques.* Boulder, CO: Brewers Publications.

Fix, G. (1999). *Principles of brewing science* (2nd ed.). Boulder: Brewers Publications.

Gorst Valley Hops. (2011). *History of Wisconsin hops*. Retrieved May 2, 2013, from http://www.gorstvalleyhops.com/history.php

Hieronymus, S. (2012). *For the love of hops: The practical guide to aroma, bitterness, and the culture of hops.* Boulder, CO: Brewers Publications.

Janson, L.W. (1996). *Brew chem 101*: *The basic of homebrewing chemistry*. North Adams, MA: Storey Books.

John I. Haas, Inc. (2009). *Barth-Haas hops companion*. Washington, DC: Independent Publisher.

Kaltner, D., Forster, C., Flieher, M., & Nielson, T. P. (2013). The influence of dry hopping on three different beer styles. *Brauwelt International*, *11*, 355-359.

Krottenthaler, M. (2009). Hops. In H. M. Esslinger (Ed.) *Handbook of brewing: Processes, technology, markets* (pp. 89). Weinheim, Germany: Wiley-VCH.

Lewis, M., & Bamforth, C. (2006). *Essays in brewing science.* New York: Springer.

Lewis, M. J., & Young, T. W. (2001). *Brewing* (2nd ed.). New York: Aspen Publishers, Inc.

Munroe, J. H. (2006). Aging and finishing. In F. G. Priest, & G. G. Stewart (Eds.) *Handbook of brewing* (2nd ed.; pp. 528). Boca Raton, FL: CRC Press.

Palmer, J. J. (2006). *How to brew: Everything you need to know to brew beer right the first time.* Boulder, CO: Brewers Publications.

Peacock, V. (1998). Fundamentals of hop chemistry. *Technical Quarterly, 35*, 4-8.

Priest, F. G. (2006). Microbiology and microbiological control in the brewery. In F. G. Priest, & G. G. Stewart (Eds.) *Handbook of brewing* (2nd ed.; pp. 608-613). Boca Raton, FL: CRC Press.

Roberts, T. R., & Wilson, R. J. (2006). Hops. In F. G. Priest, & G. G. Stewart (Eds.) *Handbook of brewing* (2nd ed., pp. 182-211). Boca Raton, FL: CRC Press.

Steele, M. (2012). *Brewing techniques, recipes and the evolution of India pale ale.* Boulder, CO: Brewer Publications.

Strong, G. (2011). *Brewing better beer: Master lessons for advanced homebrewers.* Boulder, CO: Brewers Publications.

Taylor, D. (1990). The importance of pH control during brewing. *Technical Quarterly , 27*, 131-136.

The free dictionary. (2014a). *Malster.* Retrieved from http://www.thefreedictionary.com/malster

The free dictionary. (2014b). *pH.* Retrieved from http://www.thefreedictionary.com/ph

The free dictionary. (2014c). *Specific gravity.* Retrieved from http://www.thefreedictionary.com/specific+gravity

The Hop Yard. (n. d.). *Hop's hydrocarbons*. Retrieved from http://www.thehopyard.com/hops-hydrocarbons/

United States Department of Agriculture. (2012, December 17). *National hop report.* Retrieved from http://www.usda01.library.cornell.edu/usda/current/hops/hops-12-17-2012.pdf

Wild Flower. (2013, April 30). *Hop.* Retrieved from http://www.wildflowerfinder.org.uk/Flowers/H/Hop/Hop.htm

Wolfe, P. H. (2012). *A study of factors affecting the extraction of flavor when dry hopping beers.* Oregon State University. Retrieved from http://ir.library.oregonstate.edu/xmlui/bitstream/handle/1957/34093/Wolfe_thesis.pdf