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Fruits in Craft Beer: A Study to Evaluate the Impact of Fruits on the pH in the Brewing Process and the Breweries Waste Water

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Authors' contributions

This work was carried out in collaboration between all authors. Author KD wrote the final draft and approved the final manuscript.

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ABSTRACT

Problems in the waste water treatment system of a local micro-brewery brought up the question whether fruits as additional ingredients can have a significant influence on the pH and the Chemical Oxygen Demand (COD) of the waste water. To reach an answer to this question, five batches of beer were brewed in August 2016 in the laboratory of the College of Environmental Science and Forestry in Syracuse, New York. Four of these different fruits (peaches, blueberries, banana and orange peel) were added for the secondary fermentation. Once the fermentation process was done, the beer was filtered and the retentate was diluted to simulate the cleaning process of the filter. The pH level was monitored in several steps during the brewing and the COD was measured for the simulated wash water. The latter is commonly used to express the amount of organic pollutants found in drinking or waste water. It is an indicator of the mass of oxygen consumed by a certain volume of solution and expressed in milligrams per liter.

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The evaluation of the data showed that the pH of the beer after the secondary fermentation varied between 3.82 – 4.83 and 4.43 – 6.60 in the wash water. The COD turned out to be between 1937 mg/l and 2917 mg/l in the wash water.

Keywords: pH; COD; fermentation; waste water; craft beer; fruit beer.

1. INTRODUCTION

For thousands of years beer has been brewed by men. It is a beverage strongly connected to our culture and our society. As we as a society changed and evolved over the centuries, so did beer and the way it is brewed.

The first hints of beer being brewed by our ancestors can be found in the Neolithic period around 5000 BC, when the humans began to settle down and grow crops. Since then, the consumption of beer played a dominant role in the culture and medicine [1]. Written reports of the consumption of beer can be traced back to the Gilgamesh epos which has its origin in the Babylonian culture approximately three thousand years ago [2]. Since then numerous references can be found in the cultural and religious writings of Egypt, the Hellenes, the Romans and many more. During the medieval times brewing techniques were further developed in monasteries. As outlined in Meussdoerffer, 2009 [1], it was during the Middle Ages that the brewing of beer was elevated to a privilege and a profession, officially stated in the times of Carlos Magnus. Later guilds were founded which organized and developed this profession and with it the craft of brewing. From medieval monasteries exist the first reports of hops being used as an ingredient in beer. Its stabilizing effect on the beverage was already mentioned by Hildegard von Bingen in the 12th century [3]. Hops become more and more common and finally replaced the use of 'Gruit' (a mix or single type of herbs like myrtle, rosemary and juniper). It was widely used during the Middle Ages to flavor beer. Moreover, it was the basis for the taxation in brewing during this period [4]. Later seaborne empires like the Vikings, the Hanse and the Dutch developed more stable forms of beer in order to supply their ventures and to trade over long distances. Later, strong hopped beer was introduced and production centers of considerable size evolved in Europe. Anno 1516 the 'Reinheitsgebot', a still existing Bavarian purity law, was introduced in Ingolstadt, Germany. For the first time the term 'beer' was defined. It also reduced the ingredients to malt, hops, and water. This was due to the common use of other substances like Henbane or Datura which could led to intoxication or even death if the brewer was not very careful with the dosing [5]. With the introduction of the steam machine and cooling technology, the production and storage was facilitated [6]. With these among other technical improvements the brewing process became independent from the season and the local climate. Hence, breweries started to grow to industrial scales.

By the end of the 19th century, brewing was an accepted part of the natural sciences. Microscopes were available and yeast was recognized as a living organism. New filtration systems and pasteurization were developed and had considerable impacts on the shelf- life of beer [1].

The craft of brewing was brought over from Europe to United States of America with the first settlers. Breweries evolved as they had in the 'Old World', but the Volstead Act in 1920 changed the American beer market profoundly. Only few breweries managed to survive the era of Prohibition by producing alternative, non-alcoholic products [1]. Therefore, today the production in the USA is mainly dominated by few huge brewing companies, which offer a rather in different range of beverages.

Nevertheless, during the last few decades the art of creating craft beer has prospered in the United States of America [7]. In the US, the production of craft beers has quadrupled from 2005 to 2014 [8]. Studies have shown that the target group of craft beers is comparable with a high quality product such as wine, organic food, artisan cheese and bread. Therefore, customers choose their products based on the quality rather than on the price. Moreover, this target group also possesses the necessary financial background to make craft beer a highly economical interesting area. This leads to the assumption that it will grow further in the years to come [9]. With the growth of this trend, breweries try new methods of modifying the brewing process in order to distinguish their beers from others. The modern hop technology has unlocked the potential of this plant and provides brewers with the opportunity to adjust their beers by using different hops [10]. But there are other possible ways to alter the taste of the product. Besides changes in the brewing and aging process itself, especially the use of fruits and spices has become very common among microbreweries. As such ingredients also often contribute acids and non-beer-specific components to the brewing process; this work will investigate the impact of several additional ingredients on the pH-level and the COD of the beer after the fermentation. Those factors were chosen as problems evolved in the water treatment system of an American microbrewery. Most micro-breweries discharge their water into the public sewer system, and therefore need to meet the discharge regulation imposed by the municipality for biological oxygen demand (BOD_5), COD, Total suspended solids (TSS), and pH, in order to not exceed the hydraulic and organic loading of the municipal waste water treatment facility which in general requires the influent waste water to be in a range of 100 mg/l to 400 mg/l BOD5, TSS 50 mg/l to 500 mg/l and pH of 6 to 9 [11,12].

Other authors have already proven the importance of the pH-level on beer flavor [13], on the foam stability [14] and defined very specific values for the different styles of beers [15], which are generally around the pH 4.0 Moreover, it was shown that a beers pH- level not only depends on its ingredients but also on the pretreatment of the used yeast strains [16]. Although the use of fruits has a long tradition among Belgium brewers [17], this seems to be the first study aiming at their impact on the pH and COD in the brewing process and the produced and discharged effluent water.

2. MATERIALS AND METHODS

To determine the impact of ingredients on the pH- level, five batches of beer were brewed with the same basic ingredients. They were split up into different fermenters and, after five days, the dry hops and the different fruits were added. During the first period of fermentation, the five batches evolved differently. This was assumed to be the result of the different activities of the yeast cells. The pH was measured right before the fruits were added and, after the seven days of second fermentation, the impact of the fruit itself can be measured. The fruits chosen for this study were peaches, blueberries, banana, and orange peel. All of those ingredients are frequently used by craft beer brewers. According to the recommendation of the American Homebrewers Association [18], the amounts of fresh fruits mentioned in table 1 were added to the fermenter after five days.

The basic process of brewing can be seen in the flow diagram (Fig. 1). Once the water had reached the desired temperature, the malt was added. By maintaining a stable temperature around 152°F for 60 minutes, the starch was transformed to fermentable sugar. An iodine test was used after one hour. It was determined that the transformation was complete. Then the false bottom with the grains was taken out of the stockpot and the remaining solids were extracted by sieving the mash into the boiling pot. The pot was heated up and, after reaching the boiling temperature, the liquid was boiled for 60 minutes. Hops were added in three different steps. The first ration was put in right after reaching the boiling temperature (60 min hops). After boiling for 45 minutes the second portion (15 min hops) were added and after 55 minutes the last amount (5 min hops) were added. After cooling down, the wort was transferred into the fermenter. Again a sieve was used to extract the solid remains from the hops. Upon adding the yeast, the fermentation process was started. After four days, the pH-level and the gravity were measured. As a further measurement of the aforementioned on the fifth day showed no significant changes, therefore the fruits and dry hops were added. To do this, the bananas, blueberries and peaches were shredded. The orange peel was cut into small pieces and baked in an oven in order to facilitate the extraction of the flavors.

The beer rested for seven days. During this second fermentation, it could absorb the flavors from the additional ingredients. Once done, the beer was filtered out of the fermenter. The pH was measured for both the retentate as well as for the filtered beer.

As one of the goals of this work was to learn more about the impact of special ingredients on the waste water quality; the retentate was diluted in water (see Table 4) in order to simulate the cleaning process of the filters. To assure a homogenous solution, it was stirred and then allowed to rest for 40 minutes. Afterwards, the pH and the COD of the solution were measured.

The COD was determined by using the colorimeter HACH DR 1900. We homogenized the solution and extracted a sample of 10 ml. This was centrifuged at 4100 rpm for 1 hour. In

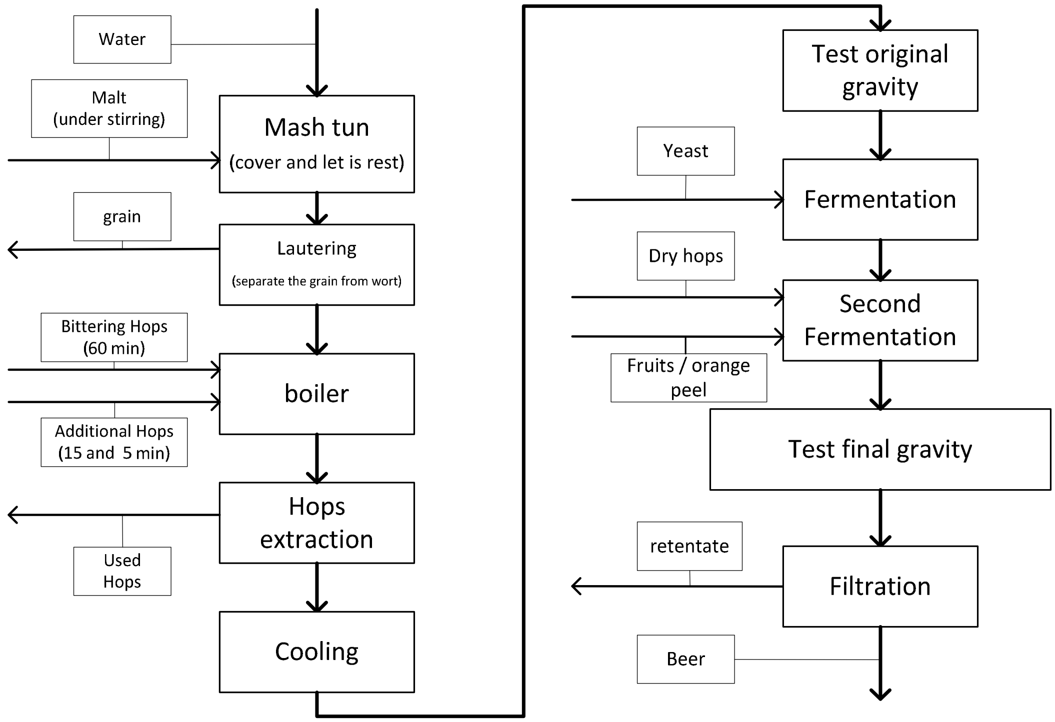

Fig. 1. Flow diagram of the laboratory brewing process

Table 1. Ingredients for different batches

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Malt	1.15 kg pale ale malt	1.15 kg pale ale malt	1.15 kg pale ale malt	2.3 kg pale ale malt	2.3 kg pale ale malt
Malt	0.25 kg cara munich cristal	0.25 kg cara munich cristal	0.25 kg cara munich cristal	0.5 kg cara munich cristal	0.5 kg cara munich cristal
Water	12l	12l	12l	24l	24l
Hops 60	7 g sterling	7 g sterling	7 g sterling	14 g sterling	14 g sterling
Hops 15	7 g sterling	7 g sterling	7 g sterling	14 g sterling	14 g sterling
Hops 5	7 g centennial	7 g centennial	7 g centennial	14 g centennial	14 g centennial
Dry Hops	7 g centennial	7 g centennial	7 g centennial	14 g centennial	14 g centennial
Fruit	853.1 g peaches	869.0 g banana	967.8 g blueberries	106.2 g orange peel	without fruit

the next step 0.2 ml of the liquid part were pipetted into a HACH Cat 24159 High Range plus COD Reagent (200 – 15,000 mg/l) test vial. After the vial was cleaned and shook, it was heated up in a HACH DRB 200 reactor for 2 hours at 150°C. In order to cool down, the vial rested overnight. The next day the colorimeter was used on program 435 COD HR at a wavelength of 620 nm. This was done three times for each sample to calculate the mean value in order to compensate the error of measurement (5%). This process was repeated with the other batches as well.

It should be mentioned that all the measurements of pH and gravity were done at a temperature of 60°F +/- 5°F. The latter was measured to determine whether the fermentation had stopped.

3. RESULTS AND DISCUSSION

The evaluation of the pH- level during the brewing process showed a considerable impact of the additional ingredients. The pH of the different fruits varied from 3.05 to 5.13. They were added into beer with a pH between 4.10

and 4.51 and resulted in a final pH from 3.82 to 4.83. As the wort was split up into five batches right after the boiling, the first fermentation took place in five different reactors. Therefore, the inhomogeneous yeast activity resulted in the slight variation of the pH before the fruits were added. Table 2 presents the measurements during the fermentation and the exact amounts of fruits used for the secondary fermentation.

As you can see in Fig. 2, the pH declined within the first days of the fermentation due to the initial growth of the yeast cells. The following autolysis stops the drop and can lead to a subsequent increase of the pH- level. The latter can be seen in the three batches peaches, banana, and blueberries. Moreover, the graph shows the impact on the pH development after the fruits were added. Depending on the pH of the additional ingredient itself, a certain trend for the further development was set. This can be seen best by comparing the pH development of the batches banana and peaches. The dried orange peels do not show a significant impact on the pH. This might indicate that the influence of liquid containing ingredients is more important than the impact of dry ingredients.

The change of the pH level during the secondary fermentation is depicted in Fig. 3. The pH was measured before the fruits were added and after the solids were filtered out. During the secondary fermentation, there was almost no change in the pH of the reference beer. The other batches showed a change in the range from -12.86% to 7.33%.

As it has been anticipated, the pH of the fruits had an direct impact on the pH development. Fruits with a lower pH than the beer (see peaches and blueberries) resulted in a lower final pH and vice versa.

Table 3 repsents the mass of retentarte which were filtered out of the beer and later diluted with approximatively 0.035 liters water per gram of retentate. The measured pH level varies from 4.43 to 6.60.

The observed low ph levels can cause negative effects on the phsical, biological and chemical waste water treatment systems at breweries or municipalities the effluent is discharged too. Therefore, neutralization to a ph level of 7.0 to 8.0 is necessary in order to avoid disruption of the treatment process for brewery effluent waste water at municipal and/or industrial treatment plants [11,19].

Table 2. pH development

	Batch 1 peaches	**Batch 2 banana**	**Batch 3 blueberries**	**Batch 4 orange peel**	**Batch 5 without**
Brewing	11 Aug. 2016	11 Aug. 2016	11 Aug. 2016	12 Aug. 2016	12 Aug. 2016
Mash pH	5.25	5.25	5.35	5.31	5.30
Start 1st fermentation	11 Aug. 2016	11 Aug. 2016	11 Aug. 2016	13 Aug. 2016	13 Aug. 2016
Check 1:	15 Aug. 2016	15 Aug. 2016	15 Aug. 2016	17 Aug. 2016	17 Aug. 2016
pH	4.17	4.14	3.63	4.25	4.22
Check 2:	16 Aug. 2016	16 Aug. 2016	16 Aug. 2016	18 Aug. 2016	18 Aug. 2016
pH	4.51	4.50	4.10	4.21	4.15
Fruit added	853.1 g peaches	869.0 g banana	967.8 g blueberries	106.2 g orange peel	No fruit
pH fruit	3.75	5.13	3.05	-	-
Final Check:	24 Aug. 2016	24 Aug. 2016	24 Aug. 2016	24 Aug. 2016	24 Aug. 2016
pH	3.93	4.83	3.82	4.30	4.19
pH solids	3.98	4.98	3.98	4.39	4.48
Change of pH	-0.58	0.33	-0.28	0.09	0.04
Change of pH in %	-12.86%	7.33%	-6.83%	2.14%	0.96%

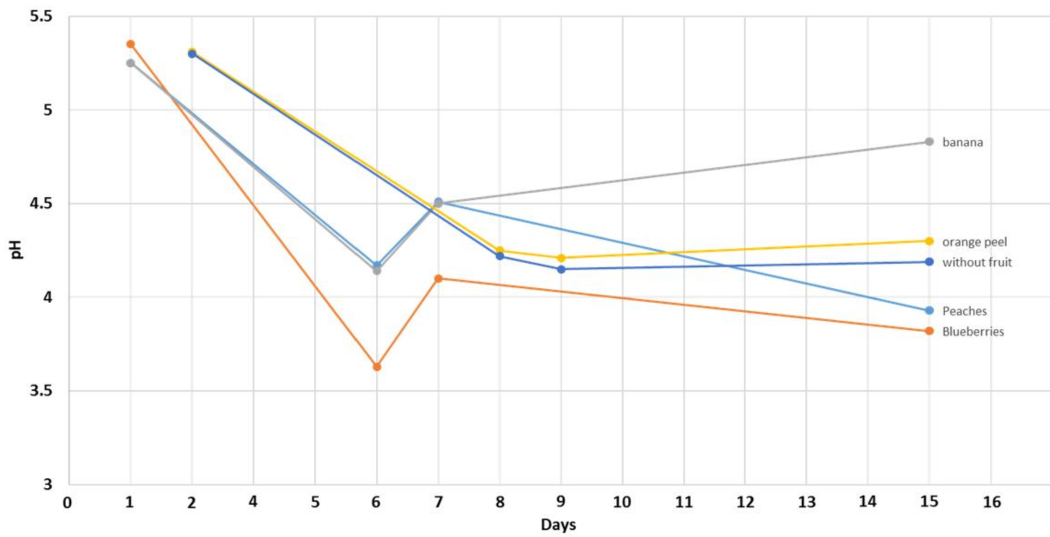

Fig. 2. Development of the pH during the brewing process

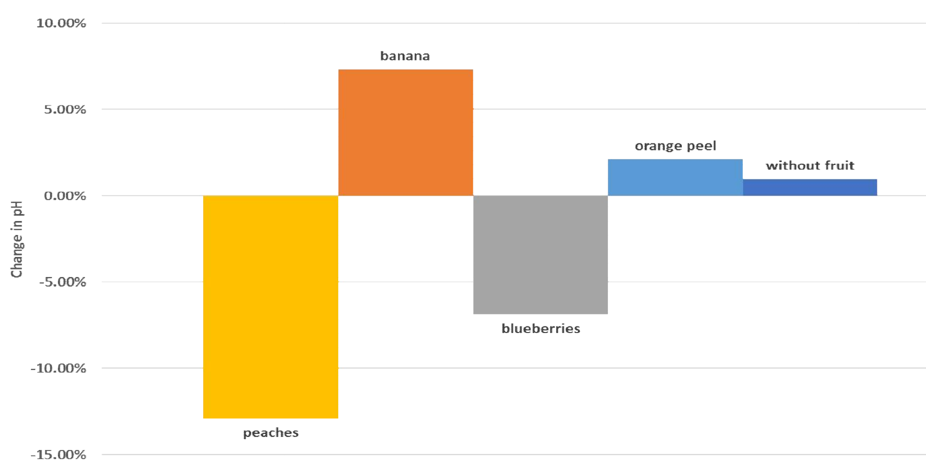

Fig. 3. Change in the pH during the 2nd fermentation

Table 3. Dilution volumes of the retentate

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Type retentate	**Peaches**	**Banana**	**Blueberries**	**Orange peel**	**Without**
Mass retentate	348.5 g	410.0 g	579.8 g	545.5 g	203.3 g
Vol. water	12 l	14 l	20 l	20 l	7 l
Ph solution	4.43	6.60	5.83	6.14	6.09

Table 4. COD measurement

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Type retentate	**Peaches**	**Banana**	**Blueberries**	**Orange peel**	**Without**
Replicate 1	2200 mg/l	2350 mg/l	2900 mg/l	2310 mg/l	1940 mg/l
Replicate 2	2200 mg/l	2350 mg/l	2920 mg/l	2330 mg/l	1940 mg/l
Replicate 3	2200 mg/l	2360 mg/l	2930 mg/l	2320 mg/l	1930 mg/l
Average	2200 mg/l	2353 mg/l	2917 mg/l	2320 mg/l	1937 mg/l

The measured COD can be seen in Table 4. It is perceivable that the brew batches containing fruits lead to a higher chemical oxygen demand between 263 mg/l to 980 mg/l in the resulting waste water compared to the conventional hops brew in batch 4. The increases can be explained with the additional organic particles which are filtered out of the beer. This indicates that the organic loading of brewery waste water needs to be taken in consideration careful for sizing of the waste water treatment system and/or discharge to municipal waste water treatment plants [11, 12, 20].

4. CONCLUSION

The evaluation of the pH level of the different types of beer showed that fruits added for the second fermentation had a perceivable impact. Nevertheless, the resulting beers had a pH between 3.82 and 4.83. This is still in a range which can be considered as normal in brewing and should not cause problems. However, ph levels that low can cause disruptions of waste water treatment operations if no pH adjustment is implemented.

Considering the COD, the measurements showed a variation from 1937 mg/l to 2917 mg/l. According to [21] the typical COD range of the waste water in a brewery is 2250 mg/l +/- 418 mg/l. Compared with this value the obtained numbers are slightly elevated. The experiment Flavoring of the beer resulted in a 10% to 30% increases the COD level which has an impact on organic loading level of the wastewater. This needs to be taken into consideration for sizing of waste water treatment operations.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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