

PEER REVIEWED SUBMISSION

# pH in Brewing: An Overview

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## ABSTRACT

The concept of pH is explained. Factors determining the pH of worts and beers are reviewed, including the nature of the buffer substances contributed from the grist, the importance of water alkalinity and hardness and the impact of yeast in fermentation. The influence that pH has in mashing is discussed, as is the relevance of pH to the quality and the stability of the finished beer.

**Keywords:** pH, water pH, acids, buffers, enzyme activity, yeast pH, mashing pH

## SINTÉSIS

Se explica el concepto de pH. Se revisarán los factores que determinan el pH del mosto y las cervezas, incluyendo la naturaleza de las sustancias reguladoras contribuidas por la malta molida, la importancia de la alcalinidad y dureza del agua así como el impacto de la levadura en la fermentación. Se discute la influencia que el pH tiene en remojo de la malta, así como la relevancia del pH en la calidad y la estabilidad de la cerveza terminada.

## INTRODUCTION

It is 92 years ago since Soren Sorensen, a 41-year-old farmer's son and Head of the Chemical Department at the Carlsberg Laboratory, introduced the concept of "pH". The term has been bandied about liberally ever since. Skin creams are advertised on the basis of their advantageous pH. Gardeners everywhere scrutinize the pH of their soil. And most everyone knows that it has something to do with acidity and alkalinity. Yet it is remarkable how few people truly understand what pH really is and what its implications are.

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Unsurprisingly for a concept first developed in a brewing laboratory, pH has long been discussed in the context of brewing performance and beer quality. Yet invariably it is addressed piecemeal, and for the effects that it has on specific issues, whether it is an impact on enzyme activity in mashing, hop utilization, yeast flocculation or product stability. In this article I seek to draw into a single repository the extant knowledge on pH.

## WHAT IS pH?

pH is simply a means for expressing the concentration of the hydrogen ion (H<sup>+</sup>) in solution.

$$\text{pH} = \log \frac{1}{[\text{H}^+]}$$

EQUATION 1

(or  $\text{pH} = -\log [\text{H}^+]$ , because in the world of logarithms to divide is to subtract)

## WATER

Water can dissociate slightly to produce the hydrogen and hydroxide ions:



EQUATION 2

Any reaction such as this, able to proceed in both directions, is characterized by an equilibrium constant which indicates the ratio of concentrations of the various components when the system is in equilibrium (i.e. when the rate of the forward reaction matches that of the reverse direction). And so the equilibrium constant for this reaction is represented by the equation

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

EQUATION 3

This equilibrium constant has been measured at 25°C and shown to be  $1.8 \times 10^{-16}$ . In other words, the vast majority of the water is undissociated.

Now the concentration of water is 55.5M. (Think about it: the molar concentration of a solute is defined as the number of moles of that substance dissolved in 1 liter of water. One mole of water = 18 g. So the molar concentration of water is  $1000/18 = 55.5\text{M}$ .)

Thus the total concentration of hydrogen and hydroxide ions in neutral water is  $1.8 \times 10^{-16}$  multiplied by 55.5, i.e.  $1.0 \times 10^{-14}$ . As they are present in equal quantities, then each is present at  $1.0 \times 10^{-7}\text{M}$  (i.e. 0.0000007M). A very small number - which is why it makes sense to talk in terms of pH. Using a logarithmic scale we arrive at a value of 7. That is, when the level of  $\text{H}^+$  is the same as that of  $\text{OH}^-$ , we have a pH of 7, or *neutrality*. If there is an excess of hydrogen ions, then we have a pH below 7 and the solution is acid. If there is an excess of hydroxide ions then the pH is above 7, and the solution is *alkaline*.

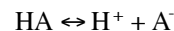
It is worth mentioning at this point that these calculations are based on values taken at 25°C. At 37°C there is more dissociation of water into its ions, and so we find that neutrality is at pH 6.8. The higher the temperature, the lower this value becomes.

Noting that pH operates on a logarithmic scale, we should realize that relatively small changes in pH mean very large differences in hydrogen ion concentration. Thus (at 25°C) a drop in pH from 6 to 5 means a ten-fold increase in hydrogen ion concentration. (If you had a ten-fold increase in, say, diacetyl concentration from 0.05 to 0.5 ppm you'd soon worry about it!) A drop in pH from 4.2 to 4.1 (as might be deemed within acceptable limits in beers, where a typical specification might have a tolerance of  $\pm 0.1$ ) represents an increase in hydrogen ion concentration from  $6.31 \times 10^{-5}\text{M}$  to  $7.94 \times 10^{-5}\text{M}$ , or 26%.

## ACIDS

It isn't only water that can dissociate to produce the hydrogen ion. Indeed any acid, by one definition, is a substance that

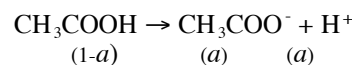
releases hydrogen ions. The stronger the acid, the more readily will it release  $\text{H}^+$ , i.e. the higher is the dissociation constant for the reaction



EQUATION 4

For acetic acid, then, at 25°C, the dissociation constant is  $1.8 \times 10^{-5}$ . For the much stronger sulfuric acid (i.e. more  $\text{H}^+$  released) the value is  $1.2 \times 10^{-2}$ .

Take a 1M solution of acetic acid. Let's say that the concentration at equilibrium of the hydrogen ion (and therefore the acetate anion) is  $a$ , then the concentration of undissociated acetic acid must be  $(1-a)$ .



EQUATION 5

Then substituting these values into the expression for acetic acid ionization we get

$$1.8 \times 10^{-5} = \frac{a^2}{1-a}$$

EQUATION 6

From this we calculate that  $a$  is 0.0042M. Bearing in mind the definition for pH, then this means that the pH of a 1M acetic acid solution is 2.38.

Henderson and Hasselbalch rearranged equations 3 and 4 for weak acids, thus:

$$\text{H}^+ = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

EQUATION 7

where HA is the undissociated acid,  $\text{A}^-$  is the anion left behind after the dissociation of  $\text{H}^+$  and  $K_a$  is the dissociation constant for the acid.

If we successively take logarithms and then multiply by -1 (making reference to the definition of pH - see equation 1), then

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

EQUATION 8

*ergo*

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

EQUATION 9

where  $pK_a$  ( $-\log K_a$ ) represents the value at which HA and  $[A^-]$  are in equal quantities ( $\log 1/1 = \log 1 = 0$ ). The lower is  $pK_a$ , the more acidic is HA. Therefore  $pK_a$  is a useful index of acid “power” – the lower the value the more acidic is a material.

## BUFFERS

The Henderson-Hasselbalch equation allows us to explain the phenomenon of “buffers”. Taking equation 4 again, it is apparent that if  $H^+$  is added to the mixture at equilibrium ( $pK_a$ ) then it will tend to react with  $A^-$  to form HA and there will be only a limited accumulation of  $H^+$  (i.e. fall in pH). Conversely if the  $H^+$  present in the equilibrium mixture is removed (e.g. by addition of  $OH^-$ ), then HA will dissociate to release more  $H^+$  in order to restore the equilibrium. Again the pH change is limited. Consequently an acid-base mixture at its  $pK_a$  comprises a buffer system capable of withstanding changes of pH, provided that additions of  $H^+$  or  $OH^-$  are not excessive. In fact a buffer operates best within one pH unit either side of its  $pK_a$ , and is best exactly at its  $pK_a$ , where the concentration of its acid (HA) and basic ( $A^-$ ) forms are identical. In other words, if you are seeking to regulate a pH to 5.0, the best buffer to select is one that has its  $pK_a$  value in that region. Fig 1 provides an illustrative example. The concentration of the buffering material is also important: the more is present, the greater the buffering potential within its buffering range. Table 1 gives some  $pK_a$  values for some of the groups found in amino acids and proteins, as well as organic acids. Thus, for example, acetic acid/acetate buffers are useful around pH 4.7.

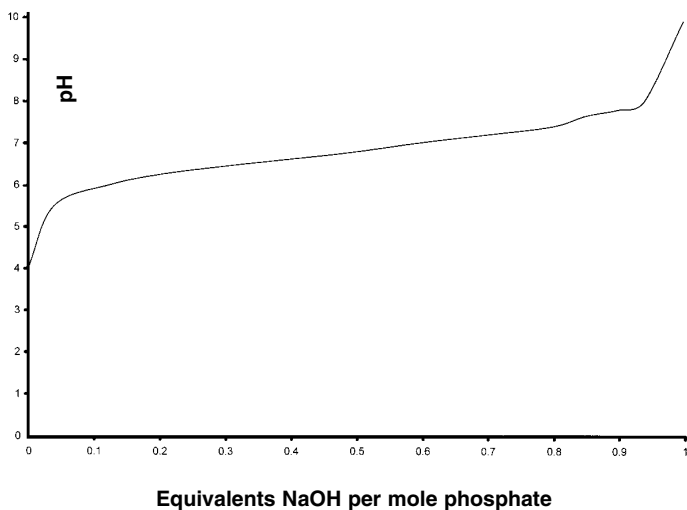


FIGURE 1

### The Titration of Potassium Dihydrogen Phosphate.

The pH change resulting from the addition of increasing quantities of sodium hydroxide to a molar solution of  $KH_2PO_4$  is plotted. Clearly such a solution is a good buffer in the pH range 6-7, but not so good at lower or higher pH's. The  $pK_a$  is the value of pH where 0.5 equivalents of NaOH have been added.

TABLE 1

### $pK_a$ values for amino acid residues and organic acids.

Residue	Amino Acid	$pK_a$ for residue in protein	$pK_a$ for free residue
$\beta$ -carboxyl	Aspartic acid	3.0-4.7	3.9
$\gamma$ -carboxyl	Glutamic acid	4.5	4.3
imidazolyl	Histidine	5.6-7.0	6.0
$\epsilon$ -amino	Lysine	9.4-10.6	10.8
Guanidino	Arginine	11.6-12.6	12.5
$\alpha$ -amino	Amino acids	-	8.6-10.7
$\alpha$ -carboxyl	Amino acids	-	1.8-2.3
carboxyl	Acetic acid	-	4.7
carboxyl	Citric acid	-	3.1, 4.8, 5.4*
carboxyl	Phosphoric acid	-	2.1, 7.2, 12.7+

\* citric acid is a tricarboxylic acid (i.e. three ionizable carboxyl groups, therefore three  $pK_a$  values);  $pK_a$  values measured at 25°C

## pH IN MALTING AND BREWING

Clearly the pH of materials such as wort and beer is determined by the concentration and type of buffer substances present, by the absolute concentration of  $H^+$  and  $OH^-$  present or introduced and by the temperature. Various materials in wort and beer have buffering capacity, notably peptides and polypeptides containing residues such as aspartate and glutamate. The  $pK_a$  of the carboxyl groups in the side chains of aspartic acid and glutamic acid residues incorporated into proteins are 3.0-4.7 and 4.5 respectively whilst the N in the imidazole group on histidine has a  $pK_a$  of 5.6-7 (Table 1). Accordingly, these groups will be important for establishing buffering at the pH range found in beers and worts. By contrast, the amino and guanidinium groups in lysine and arginine have much higher  $pK_a$  values and will be largely protonated in the pH range 4-6.

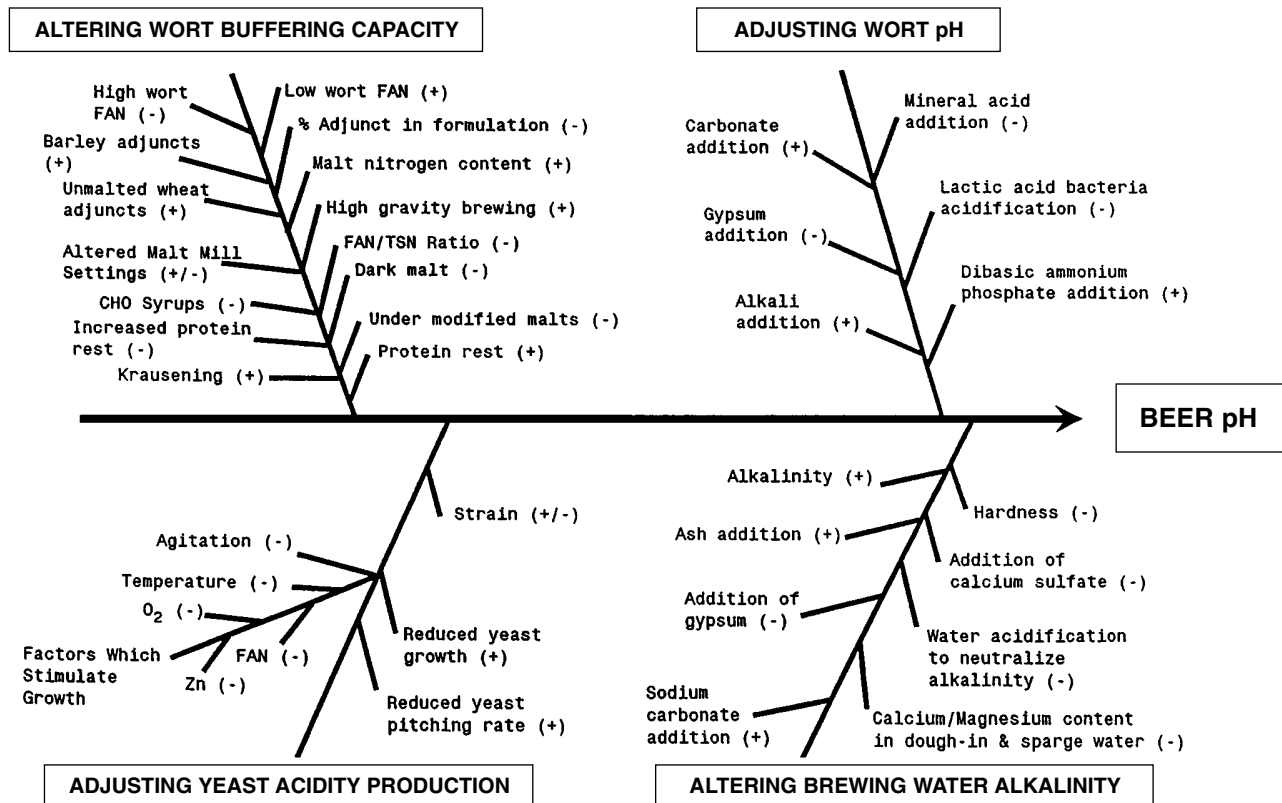
Factors promoting the level of these materials in wort will elevate the buffering capacity. Such factors will include the nitrogen content of the malt, its degree of modification and the extent of proteolysis occurring in mashing. As certain adjuncts, such as sugars, do not contain peptides and polypeptides, their use will tend to lessen the buffering capacity of wort.

The buffering capacity of a wort or beer can be readily assessed by adding acid or alkali to beer and assessing the extent to which measured pH changes [57].

$$\text{Buffering Capacity} = \frac{\text{Concentration of } H^+ \text{ or } OH^- \text{ added}}{\text{Change in } H^+ \text{ concentration observed}}$$

EQUATION 10

Hammond [24] reported that the buffering capacity of worts and beers are very similar at pH's below 5.5. In beer the buffers are mostly of low molecular weight (<2,000 in molecular weight) and fall into the categories of peptides and organic acids.



NB (+) = as the factor increases, so too does beer pH; (-) = as the factor increases beer pH decreases

FIGURE 2

A Summary of factors that may impact the finished pH of beer.

In turn, the pH impacts on the chemistry happening in all process stages in malting and brewing and the finished beer.

The complete range of pH practically encountered in brewing is from 3 in lambic-style beers to around 6 for some paler worts [57]. Hereinafter I will describe the impact that the raw materials and various process stages can have on beer pH and, in turn, the impact that this has on product quality. Fig 2 is a fishbone diagram summarizing the factors impacting on pH.

## BARLEY, MALTING AND MASHING

When searching the literature, the reader should be cautious about the pH values quoted and inferences made about their impact, because the temperature is not always quoted. The pH of wort, for instance, will be of the order of 0.34 lower at 65° C than at 18° C because of increased dissociation of acidic materials [27].

Extracts of barley have pH's of 6.65-5.83 [38]. The pH of such extracts produced after steeping is lower by 0.35-0.66 units, because buffer substances have been leached from grain [38]. Microflora populating the surface of barley contribute to a lowering of pH. Deliberate seeding of the grain with lactic acid bacteria and the attendant lowering of pH have been employed for the prevention of growth of undesirable organisms in malting [23]. The pH rises as a result of modification during germination [26].

Consequently the pH range in green malt is 5.8-6.2. Factors limiting embryo activity tend to lead to lower malt pH's.

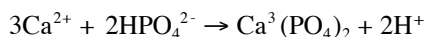
The pH falls again during kilning. Higher initial moisture contents before kilning and higher kilning temperatures give lower pH. The pH falls by 0.2-0.4 with even, gentle kilning and may fall a further 0.2-0.3 at progressively higher temps [37]. Therefore, ale malts tend to have lower pH values than do lager malts. In the cause of reducing nitrosamine levels, the surface pH of malts prior to kilning may be lowered (typically a pH of <4.0 is sufficient) using acids (e.g. sulfuric) or sulfur dioxide [59].

We should remind ourselves that the net pH observed is a consequence of the endogenous pH within the unmilled malt but also of chemical changes taking place during the extraction process. Thus, for example, it has been shown that the pH is 0.1-0.15 lower in worts derived from decoction mashing than those from infusion mashing [38].

South [53] found significant variability of pH between malt batches, with a fall in winter months and subsequent rise. This was linked to differences in lactate levels. He went on to suggest that this lactate is primarily produced by embryo metabolism in steeping, but by grain microbes later in germination and kilning [54].

Apart from the grist and the temperature, the other factor influencing the pH in mashes is the water. Harder water renders pH's as much as 0.3 units lower than those made with soft water.

Taylor [57] reports a lowering of pH in wort from 5.51 to 5.1 by increasing the level of calcium from 50 to 350 ppm. Calcium reacts with carbonate, phosphate and polypeptides to promote the release of protons and thus lowering of pH. For example



EQUATION 11

Thus the level of such materials present is important, including alkalinity in respect of carbonates and bicarbonates.

The other concept used in describing the alkalinity of water is “residual alkalinity” which is of particular importance in correct adjustment of pH. Fundamentally, residual alkalinity combines in a single term the relative levels of the two key determinants of pH in water, namely the total alkalinity (i.e. level of alkaline substances, notably bicarbonate, as determined by titration) and the level of hardness (as determined from the level of the calcium and magnesium).

$$\text{Residual alkalinity} = (\text{Bicarbonate}) - \left( \frac{\text{calcium}}{3.5} + \frac{\text{magnesium}}{7.0} \right)$$

EQUATION 12

(The concentrations are quoted as mval’s, i.e. milliequivalents per liter. The equivalent weight of a material is its molecular or atomic weight divided by its valence.)

Bicarbonate serves to increase pH, whereas calcium and magnesium lower it through their interactions. The higher the residual alkalinity, the greater the total alkalinity relative to hardness and so the higher the pH. It will be appreciated that two waters might be identical in terms of inherent alkalinity (e.g. the waters of Burton-on-Trent and Munich have very similar bicarbonate levels and therefore alkalinity) but very different in respect of residual alkalinity (Burton water contains far more calcium and magnesium than does the Munich equivalent).

According to Taylor [57], mashing is the critical stage in respect of determining the pH of wort and beer for the impact that it has in determining buffering capacity.

## pH AND ENZYME ACTIVITY IN RELATION TO MASHING AND WORT

There have been surprisingly few (if any) detailed studies of the precise impact of pH on mashing performance and wort composition. Textbooks of brewing make reference to “optimum” pH’s for parameters such as extract and “wort filtration”, though they are conspicuous by the lack of references. One textbook refers to a previous textbook! It seems that a largely empirical approach has been employed. How the data has been generated and on what scale (lab mashes are not always good mimics of commercial mashes) is unclear. Furthermore, the manner by which the pH has been adjusted in such studies is seldom apparent, despite its tremendous importance. For example, in my own laboratory we demonstrated that different performance was observed in small-scale mash filtrations depending on whether the pH was adjusted by using mineral acids, lactic

acid or calcium [3]. Apart from an influence on pH, the different agents may affect the system in other ways. For instance the calcium ion can bind to all manner of materials other than phosphate, including oxalic acid and proteins. Accordingly it could have a profound effect on things such as grain particle size, thereby influencing wort separation in ways other than by impact on pH.

It is believed that there is in effect a “circular” significance of enzyme in relation to pH insofar as phosphatases in malt attacking phytic acid (phytase) and the repeating units in nucleic acids (nucleotide phosphatases) are responsible for releasing phosphate, which in turn reacts with calcium to presage a pH drop [16]. There again, Kunze [31] says that lowering the pH of a mash by acidification increases phytase action and the released phosphate raises the buffering capacity. Ergo, it is important not only to acidify the mash, but also the wort.

Kunze [31] suggests that the “optimum” pH for a mash is 5.5-5.6, in respect of attenuation limit, protein breakdown, viscosity, lautering rate and restriction of color increase (the higher the pH, the greater the extraction of coloring materials).

Table 2 shows some of the quoted data for the impact of pH on mashing parameters. Although there are clearly differences (most notably in the observations on mash filtration), both compilations indicate that the pH for maximum fermentability is slightly higher than that for maximum extract. Luers [35] suggests that for lager malts no difference in extract and saccharification time occurs over the pH range 5.6 - 6.0 but Kolbach [30] says that extract yield may be low at higher pH’s. Hence the promotion of acidification using sulfuric, hydrochloric or lactic acid additions or naturally through the agency of lactic acid bacteria. Gorff et al [17,18] detail an investigation into the impact of mash and wort acidification. There is no major impact on final beer pH [39]. Luers [35] observed that wort filtration is most rapid at 5.5-5.75.

TABLE 2

The impact of pH in mashing.

	Briggs et al. [8]	Bamforth & Simpson [3]
Highest Extract yield	5.2-5.4	5.3-5.8
Highest Fermentability	5.3-5.4	5.4-5.8
Fastest Wort Filtration	“mash impossible to filter <4.7”	4.4-4.6
Highest Total Soluble Nitrogen	4.6	4.7-5.0
Highest Free Amino Nitrogen	4.6	4.7-5.2

This concurs with the observations of others [31]. When calcium was used to adjust mash pH, however when pH was adjusted by direct addition of sulfuric, hydrochloric or lactic acids, then the “optimum” for mash filtration was much lower (4.4-4.6). Perhaps this explains the discrepancy reported between this study and the results summarized by Briggs et al [8] (c.f. Table 2), viz. it is not only the pH *per se* which influences a parameter such as wort filtration, but also the agent used to adjust the pH (see earlier).

Reference to Table 3 shows the quoted “pH optima” for the key enzymes of mashing. Interpretation of the data for some enzymes is rendered difficult by the selection of “unnatural”

substrates. For instance, Wrobel & Jones [60] showed that the proteolytic activity of extracts of green malt is highest at pH 3.8 when hemoglobin was used as substrate, but extends over the range 4.7-6 if gelatin were the substrate. For a hordein substrate, activity was similar over the entire range from 3.8 to 6.5. Another important note is that most enzymes display considerable activity either side of their pH optimum. Provided they survive long enough in the mash, they may be able to complete their job even when not operating at pH optimum. Actually, the impact of pH in a mash will be more than on the relative rates of the reactions catalyzed by the various enzymes. pH will influence the stability of the enzymes, also, as well as having a bearing on other non-enzymic issues, e.g. solubility and extractability of materials. Thus, it would be surprising if a simple model could be constructed relating pH optima for enzymes to mashing performance and wort composition. It is likely that

**TABLE 3**  
**pH "optima" for malt enzymes**

Enzyme	pH optimum	reference
Amino-peptidase (neutral)	7.0, 7.2	[15]
Amino-peptidase (leucine)	8-10	[15]
$\alpha$ -amylase	5.5	[19]
$\alpha$ -amylase I	3-5.5	[6]
$\alpha$ -amylase II	5-5.4	
$\beta$ -amylase	5.2	[43]
Carboxypeptidase	4.8, 5.2, 5.6	[15]
Dipeptidase	8.8	[48]
$\beta$ -glucan endohydrolase	4.7	[15]
$\beta$ -glucan exohydrolase	5.25	[28]
$\beta$ -glucan solubilase	6.35	[4]
$\alpha$ -glucosidase I	5.6	[55]
$\alpha$ -glucosidase II	6.3	
$\alpha$ -glucosidase	4.5	[36]
Limit dextrinase	5.5	[41]
Lipase	6.8, 8-8.5	[5]
Lipoxygenase	6.5	[14]
Maltase	4.2	[55]
Endo-peptidase - SH	3.9, 5.5	[15]
Endo-peptidase - Metal	5.5, 6.9, 8.5	[15]
Peroxidase	3.25-3.75	[9]
Phytase	5 - 6	[34]
Superoxide Dismutase	Activity at wort pH's	[2]

heat tolerance of the various enzymes is of far more significance. One impact of pH seldom studied is its influence on the actual extractability of enzymes. In one such study, MacGregor & Lenoir [36] showed that only about 50% of the  $\alpha$ -glucosidase extractable at pH 7.5 is actually brought out of malt in the range of normal mash pH's. Stenholm & Home [56] presented evidence to suggest that the benefit of lowering mash pH from 5.7 to 5.4 benefits starch degradation not by promoting amylase activity but rather by enhancing the extractability of limit dextrinase.

One of the more authoritative studies of the impact of pH on mashing performance is given by Taylor [57]. He showed that when the level of calcium is low, there is a sizeable increase in wort pH during run-off, especially as gravity decreases. Such

increases in pH lead to increased extraction of materials such as silicate and polyphenol into the wort [10]. The concentration of calcium needs to be 100-200 ppm in both mashing and sparge water if excessive pH rise is to be avoided. This will of course be impacted by gravity and the nature of the grist. Taylor [57] reported that the worts resulting from these higher calcium mashes had higher extract, higher free amino nitrogen and higher mash bed permeability. The last of these was claimed to be a consequence of less of the fine materials in the spent grain bed (gel proteins?) that impede wort flow. Again it is important to stress that these effects may not have been solely due to a change in pH, but at least in part due to some other impact of calcium.

## WORT BOILING

The pH of wort drops about 0.3 units during boiling [38]. Lower gravity worts have a higher pH before boiling, but a substantially bigger pH drop on boiling. Whereas the differences in pH of mashes over the range of gravities 7.5 - 20 degrees Plato is relatively constant, final wort pH's are progressively lower as the gravity increases [11]. The range encountered was a pH of 5.8 for a 7.5°P wort with no Ca supplementation to 5.45 for a 20°P wort mashed with an addition of 1 g/L gypsum.

The recovery of bitter substances is higher at higher pH's in starting wort, *ergo* hop utilization is better in lower gravity worts. Hop bitter compounds and their derivatives are weak acids that are more soluble at high pH values than at low ones. Kunze [31] recommends adjustment of wort pH to 5.1 - 5.2 by acidification approximately 30 minutes before the end of boiling, to allow prior time for isomerization to be effected.

pH has a substantial effect on the clarification of wort. Worts of pH below 4.5 completely fail to fine, and a pH of 5.0 is needed for efficient settling [32]. Increasing the wort pH by as little as 0.1 - 0.3 pH units leads to a situation where less kettle finings (carrageenan) need to be used to promote clarification [33]. This is contrary to expectation, since the proteinaceous material to be removed would be more positively charged at lower pH's and presumably better able to react with the negatively charged Irish moss. Leather et al. invoke the likelihood of a bridging of the two negatively charged molecules through metal cations to explain the observation [13]. Alternatively, it is possible that the higher pH is leading to a conformational change in one or other species to generate a molecular shape better able to lead to interaction or precipitation [33]. Whatever is the explanation, these observations are a salutary illustration of the impact that a seemingly modest change in pH can have.

## FERMENTATION

pH falls during fermentation as a result of the consumption of buffering materials (free amino nitrogen) by yeast and the release of organic acids. Coote & Kirsop [12], however, found a similar buffering capacity in wort and beer and calculated that the removal of buffering materials and release of organic acids are insufficient to account for the magnitude of the pH drop in fermentation. They concluded that the direct excretion of H<sup>+</sup> by yeast accounts for the discrepancy. Factors promoting vigor and growth of yeast in fermentation will stimulate proton excretion and pH drop.

Lager worts and beers have somewhat higher pH values than do ales: MacWilliam<sup>[38]</sup> cites ales with pH's in the range 3.8–4.2 and lagers in the range 4.2–4.75.

There is a balance to be struck in the relationship of free amino nitrogen to pH. If levels of FAN are too low, then reduced buffering potential is present. However, too much FAN stimulates yeast growth excessively, with attendant release of organic acids and H<sup>+</sup> and lower pH in beer. Other factors promoting yeast growth (e.g. increased oxygen levels and zinc) will also tend to cause a lower beer pH. An increase in pH at the end of fermentation indicates autolysis.

The converse consideration of pH in the context of yeast is the removal of contaminating bacteria by the use of acid washing. Simpson & Hammond<sup>[51]</sup> have stressed that brewing yeast is remarkably resistant to acid environments but emphasized the protocols that should be used to prevent damage to yeast.

Actually, adjustment of wort pH has relatively little impact on beer pH<sup>[57]</sup>. The critical factors are the buffering power that survives the fermentation and the extent to which acid/H<sup>+</sup> is produced during fermentation.

High gravity brewing can lead to higher beer pH's after final dilution. For example Pfisterer and Stewart found pH's of 4.55 and 4.10 in finished lagers with starting gravities of 17.65 and 11.93° Plato respectively<sup>[46]</sup>. The beers brewed at the higher gravity had better colloidal and flavor stability. Great care must be exercised with the dilution water when diluting worts derived from high gravity brewing<sup>[22]</sup>: their level of residual alkalinity and buffering capacity will impact on the pH of the finished beer.

pH influences the flocculation behavior of yeast<sup>[47,58]</sup>, the net level of surface negative charge dictating the opportunity for intercellular bridging via divalent cations. pH also profoundly influences the ability of beers to fine and yet it does not appear to have been possible to define the precise relationship between pH and finability<sup>[32]</sup>.

pH can have a sizeable impact on the production of flavor components by yeast. A shift in pitching wort pH from 5.75 to 5.46 led to a halving of dimethyl sulfide production during fermentation<sup>[1]</sup>. The rate of conversion of acetolactate to diacetyl increased by a factor of 4 when the pH in fermentations was lowered from 5.5 to 4.0<sup>[25]</sup>.

## BEER

As beer pH decreases over the typical range from 4.5 to 3.9 there is

- increased resistance to microbial spoilage
- increased colloidal stability (for reasons not fully understood)
- increased foam stability (for reasons not fully understood,<sup>[42]</sup>)
- decreased flavor stability
- (possibly) decreased palate smoothness and drinkability

Brenner et al.<sup>[7]</sup> say pH affects the quality of bitterness. Rigby<sup>[48]</sup> claims that bitterness is harsher at higher pH values. However Simpson et al.<sup>[52]</sup> found no impact of pH on the flavor threshold of isohumulone.

Simpson<sup>[50]</sup> showed that the antimicrobial activity of hop bitter compounds is much greater when they are in their uncharged forms, at low pH, pK<sub>a</sub> values for the iso- $\alpha$ -acids are of the order of 3.

Grigsby et al.<sup>[20,21]</sup> demonstrated that the tendency of beer to oxidize is less at higher pH's. Nordlov and Winell<sup>[44]</sup> suggest that this can be explained in terms of the impact of pH on the dissociation constant for the adducts formed between staling carbonyl compounds and sulfur dioxide, but Kaneda et al.<sup>[29]</sup> invoke the role of pH in protonating the superoxide radical to form the much more damaging perhydroxyl species. The pK<sub>a</sub> for this interconversion is 4.88.

Pellaud et al.<sup>[45]</sup> observe that at a given temperature the major parameter influencing the precipitation of oxalate is pH: at pH 4.5 as compared to 4.0 there is a far greater opportunity for calcium to precipitate oxalic acid.

Taylor<sup>[57]</sup> looked at the impact of pH on flavor by altering pH through addition of acids. At low pH (< 4) beers became more *sharp*, with an increased *drying* character in the after-taste and an increased perceived *bitterness*. At pH's < 3.7, there was a *metallic* after-palate, while especially at pH > 4.4, *soapy* and *caustic* notes were reported. Higher pH's were accompanied by comments about *mouthcoating*, *biscuit* and *toasted*.

Siebert<sup>[49]</sup> highlights that it is not simply a role for organic acids as a supplier of H<sup>+</sup> that causes their sourness impact, but that structural features of these molecules also determine their flavor threshold.

## CONCLUSION

One might have anticipated that, by now, the appreciation of the precise effects that pH can have on the brewing process and beer quality and also the exact materials that determine the pH of wort and beer would be set in tablets of stone. This is not so, at least in part because of the complexity of the matrices involved. Although there is a clear supposition about the major buffering substances in beer, there is not an authoritative account of the relative contribution made by various nitrogenous and other materials. There is a consensus that pH has a direct bearing on flavor stability, foam stability and colloidal stability, yet no fully documented rationale for these effects. Much remains to be researched in the world of pH and brewing.

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