# The Importance of pH Control During Brewing

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## ABSTRACT

There is a tendency for pH of wort and beer to be accepted as a consequence of brewhouse and fermentation procedures, rather than emphasis being placed on the mechanisms for pH control representing a major element of brewing process control.

The control of pH during wort production has significant impact on brewhouse performance and wort composition. Data has been compiled from small-scale experiments and production trials to illustrate the impact of pH variation on extract recovery, wort protein and carbohydrate content and mash bed permeability.

Mechanisms determining pH control during fermentation have been investigated and the influence of wort composition in terms of amino acid/small peptide composition on beer pH and potential haze stability and head formation has been explored on laboratory-, pilot-plant and production-scale. The results obtained have allowed conclusions to be made regarding the relative significance of factors stimulating yeast growth and wort buffering capacity on beer pH, and consequent influence on beer flavor and stability.

## SINTÉSIS

Existe una tendencia de aceptar el pH en mosto y cerveza como una consecuencia del procedimiento de cocimiento y fermentación, en vez de darle énfasis a que los mecanismos para controlar pH representan un elemento principal del control del proceso de cervecería.

El control de pH durante la producción de mosto tiene un impacto significante en el comportamiento de la sala de cocimiento y en la composición del mosto. Se ha reunido data de experimentos a pequeña escala y de pruebas de producción para ilustrar el impacto de variaciones del pH en recuperación del extracto, proteína en mosto y contenido de carbohidratos y permeabilidad de la cama de malta macerada.

Los mecanismos que determinan el control del pH durante fermentación han sido investigados y la influencia de la composición del mosto en términos de amino acido/péptido pequeño en la composición del pH en cerveceza y el potencial de estabilidad de turbidez y formación de espuma han sido explorados en escalas de laboratorio, planta piloto y producción. Los resultados obtenidos han permitido llegar a conclusiones respecto al significado relativo de los factores estimulando crecimiento de levadura y la capacidad de amortiguación del mosto en el pH de cerveza y consecuentemente su influencia en el sabor y estabilidad de la cerveza.


## INTRODUCTION

Control of pH throughout the brewing process, from mashing-in to final packaging, is fundamental to the achievement of end product consistency.

The importance of control of finished beer pH is well accepted since the influence of pH on beer flavor, physical and microbiological stability is clearly recognized.

However, the maintenance of consistent pH throughout wort production, fermentation and conditioning is equally important to beer quality, by ensuring reproducible conditions for the numerous enzymic and chemical reactions occurring during these beer production stages. Somewhat perversely, it is not uncommon for wort and in-process beer pH values to be accepted as a consequence of brewhouse and fermentation procedures, rather than mechanisms for pH control being regarded as major elements of brewing process control.

It is possible that any lack of awareness of pH control procedures may have arisen because of the very nature of the pH scale itself, because of a tendency to overlook its logarithmic basis.

Sørensen in 1909 devised the concept of expressing hydrogen ion concentration in terms of the negative logarithm (pH). This is a much more convenient way of considering the full range of possible hydrogen ion dissociation in aqueous solutions (i.e., as low as of $10^{-14}$ gm ions/liter, being more conveniently expressed on a linear scale up to 14).

Arguably, in conventional brewing terms, the effective range of hydrogen ion concentration of interest is only $10^{-3}$ to $10^{-6}$ gm/liter (i.e., pH 3.0 to pH 6.0), which would cover the lowest likely beer pH (as in Belgian 'Lambic Beer') to the highest likely wort pH value.

The somewhat misleading nature of the logarithmic scale can be exemplified by considering a working wort pH specification of 5.4 (range 5.2 to 5.6) and a beer pH specification of 4.0 (range 3.8 to 4.2). The wort range (5.2 to 5.6) equates to a variation in hydrogen ion concentration of 6.3 to 2.5 μgm/liter (i.e., 3.8 μgm/liter), while the beer range (3.8 to 4.2) is equivalent to 159 to 63 μgm/liter (i.e., 97 μgm/liter). These wort and beer pH ranges could be regarded as acceptable in-process tolerances (i.e., ± 0.2 pH units), but actually represent target hydrogen ion concentrations of 4.0 μgm/liter, plus 58% and minus 37% (for wort pH 5.4 ± 0.2) and 100 μgm/liter, plus 60% and minus 37% (for beer pH 4.0 ± 0.2) respectively. Expressed as hydrogen ion concentration, these variations represent much wider ranges than would normally be tolerated for other key beer quality parameters.

Consequently, there clearly is a strong requirement to be aware of all factors influencing pH control. The results presented here have been obtained from a program of investigations into the impact of pH variation on brewhouse performance and wort composition (particularly soluble nitrogenous components, such as amino acids) and on the mechanisms of pH control during fermentation (influenced by wort soluble nitrogen content), carrying through to finished beer pH control and potential haze stability and head formation ability.

## EXPERIMENTAL

In addition to assessments of standard, and laboratory-modified, production worts and beers, results were obtained from small-scale mashing and fermentation systems and pilot-scale brewing trials.

### Flavor Effects

Organoleptic assessments were carried out on beers of measured varying pH and of beers obtained by pilot-scale experiments to adjust beer of standard composition to a range of pH values, by addition of equimolar proportions of dilute hydrochloric and sulphuric acids or by addition of a dilute solution of sodium carbonate.

### Wort Production Trials

A 10-liter scale mashing and lautering system was used for investigating influences of pH control during wort production.

The design and operation of this experimental system has been described previously [1]. The system provides a procedure for production of wort (up to 10 liters) under controlled, reproducible conditions, to allow assessment of the influence of variation of a number of mashing and lautering parameters on wort composition.

By operating the lautering column at constant wort flow rate and by monitoring mash bed depth and differential pressure across the mash bed, with respect to time, a reproducible system for estimating mash bed permeability can also be established.

### Fermentation Trials

Laboratory-scale fermentations were carried out either in 10 liter stainless steel and glass cylindro-conical vessels (each equipped with full temperature control through two side-wall, plus cone cooling jackets) or in 5 liter, stirred-pot glass fermenters, housed within temperature-controlled water baths (equipped with six separate, constant speed, stirring positions).

Experiments were designed to carry out parallel fermentations of standard, 1040 ° gravity (10 °P) wort under defined conditions, allowing assessment of the influence of variation of a number of wort composition parameters.

Parameters investigated included:

- wort dissolved oxygen level
- wort zinc content (up to 0.3 ppm)
- wort pH; varied by addition of various acids (including amino acids) and of sodium carbonate.
- wort FAN (free $\alpha$ - amino nitrogen) content; varied by dilution of 1040 ° wort with 1040 ° glucose syrup and/or supplementing the amino acid content by addition of 0.5% (w/v) solutions of either an equimolar mixture of Serine, Leucine and Glycine or an equimolar mixture of Aspartic acid, Leucine and Glycine. (These amino acids were selected as representing the groups readily utilized by yeast, as classified by Jones and Pierce [2]; Serine and Aspartate-Group A, Leucine-Group B, Glycine-Group C.)

### Conditioning Trials

Standard production pilot-brewed beer was adjusted, from pH 4.0, after 6 days cold storage at 0 °C, to various pH values by addition of solutions of sodium and/or calcium carbonate.

100 liter batches of adjusted beers were stored at 0 °C for 4 hours, prior to filtration under standard conditions and bottling for storage trials.

### Other Analyses

Buffering capacity is defined as the numerical ratio of:

$$\frac{\text{Total concentration of H+ (or OH}^-\text{) ions added}}{\text{Change in H+ concentration observed}}$$

This was estimated in worts and beers by titration in the pH range 4.0–5.0, by the measured addition of standardized acid (HCl) to worts (after adjustment to pH 5.0) and of standardized alkali (NaOH) to beers (after adjustment to pH 4.0), to effect the required change in hydrogen ion concentration (viz 100 to 10 μgm/liter; ie 90 μgm/liter).

## RESULTS

### pH Control During Wort Production

*Effect of Liquor Composition*

The concentration of calcium ions and carbonate ions in water used as mash liquor has considerable influence on pH of collected wort, as indicated in Table 1.

These results were obtained from mashes using a single batch of malt, a mash thickness of 3:1 (liquor to grist ratio), with liquors containing the indicated levels of calcium ion (added as gypsum) and carbonate ion (added as sodium carbonate), and monitoring the pH values of wort (cooled to 20 °C) at 1040 ° gravity (10 °P) before and after boiling for 60 minutes (and adjusting to 1040 ° gravity).

Addition of calcium ions reduces wort pH and is antagonistic to the effect of carbonate ions to increase wort pH.

*Effect of Calcium Content on Wort pH During Mashing*

The results presented in Fig. 1 refer to operating the mashing and lautering experimental system at a mash thickness of 3:1 (liquor to grist), with mashing and sparging liquors prepared from aqueous solutions of gypsum to give the indicated calcium contents, and monitoring the pH value of wort at discrete points during run-off.

It can be seen that at low calcium contents, wort pH increases considerably during run-off, especially as the wort gravity decreases, particularly towards the end of run-off. A calcium content in mashing and sparging liquor of 100–200

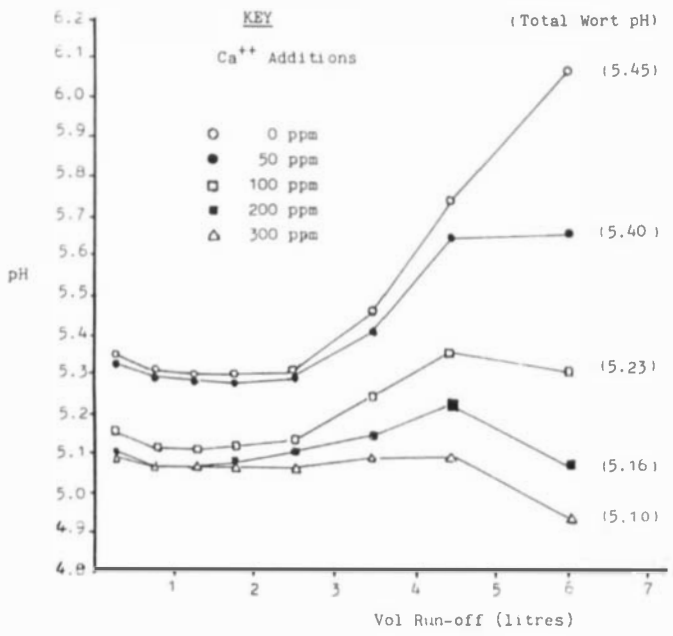


**Fig. 1 pH change during wort run-off as a function of mash liquor calcium content.**

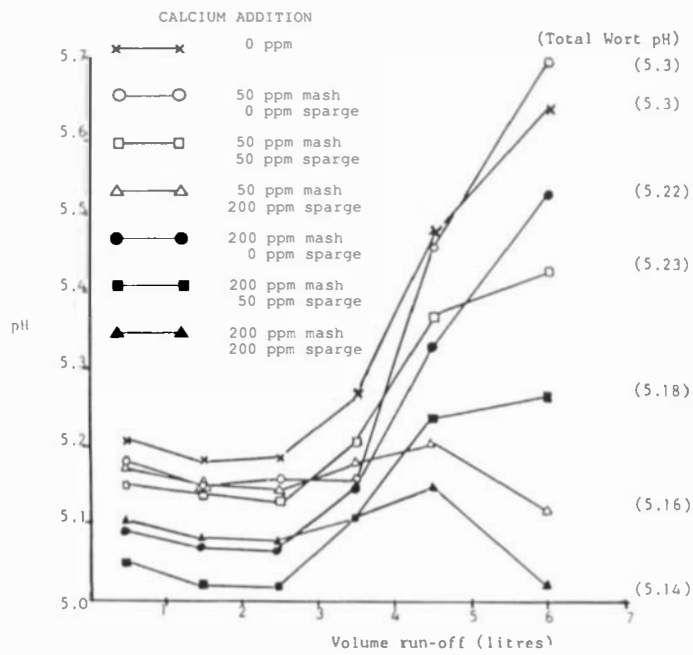


**Fig. 2. pH changes during wort run-off as a function of various mashing and sparging liquor calcium contents.**

**Table 1**
**Effect of Mash Liquor Composition on Wort pH**

| Liquor | Wort pH | |
|---|---|---|
| | Pre-Boil | Post-Boil |
| 50 ppm $Ca^{2+}$ | 5.51 | 5.36 |
| 350 ppm $Ca^{2+}$ | 5.10 | 5.00 |
| 50 ppm $Ca^{2+}$ + 100 ppm $CO_3^{2-}$ | 5.80 | 5.65 |
| 350 ppm $Ca^{2+}$ + 100 ppm $CO_3^{2-}$ | 5.44 | 5.28 |

ppm is required to maintain consistent pH throughout wort run-off.

As expected, the pH of the total collected wort decreases, with increasing calcium content.

*Effect of Varying Calcium Content of Mashing and Sparging Liquors on Wort pH*

The results presented in Fig. 2 were obtained by operating with sparging liquors of varying calcium content, relative to mashing liquor.

The pH values observed during lauter run-off at varying levels of calcium indicate that a relatively high level of calcium is required in the sparging liquor to ensure consistent pH control throughout wort run-off.

*Effect of Mash pH on Wort Composition*

Analyses of worts collected from the experimental trials in Fig. 1, are listed in Table 2.

It can be seen that as wort pH decreased, as a consequence of lower pH values during mashing due to higher calcium contents, recoverable extract increased, and levels of wort nitrogenous components increased (measured as total soluble nitrogen—TSN and free-$\alpha$-amino nitrogen—FAN).

*Effect of pH on Mash Bed Permeability*

Also recorded in Table 2, and displayed in Fig. 3, are measurements of mash bed permeabilities, observed in the series of mashing and lautering experiments described above.

Clearly reduced pH during mashing has resulted in increased mash bed permeability.

Coincident with this increased mash bed permeability, it was observed that various parameters, indicating an increased degree of proteolysis during mashing and/or reduced degree of association of polypeptide molecules, also correlated with lower mash pH. As shown in Fig. 4, the ratio of FAN:TSN content in the collected wort increased as mash pH decreased;

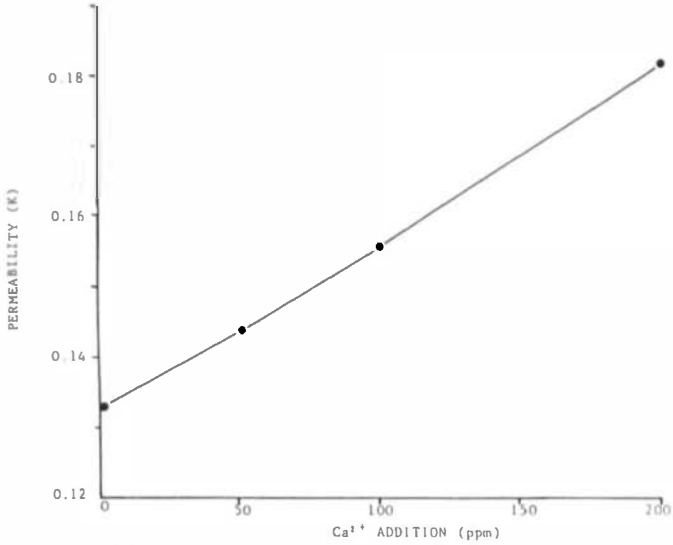


**Fig. 3. Relationship between mash bed permeability and mash liquor calcium content.**

**Table 2**
**Wort Composition Related to Increasing Mash Liquor Calcium Content**

| | Calcium Content (ppm) | | | |
|---|---|---|---|---|
| | 0 | 50 | 100 | 200 |
| pH | 5.45 | 5.40 | 5.23 | 5.16 |
| Extract (L°/kg) | 298.2 | 289.1 | 300.3 | 302.4 |
| Apparent Fermentability (%) | 87.3 | 88.6 | 87.7 | 86.1 |
| TSN (ppm) at 1040° | 873 | 904 | 931 | 950 |
| FAN (ppm) at 1040° | 168 | 184 | 189 | 191 |
| Mash Bed Permeability | 0.130 | 0.145 | 0.155 | 0.180 |

the content of high molecular weight polypeptide (i.e., greater than $5 \times 10^3$ daltons, as measured by staining with Coomassie Brilliant Blue[3]) decreased and finally the proportion of 'fine' particles remaining in the spent grains after run-off (measured from the volume of fine material separable from the exhausted mash bed after resuspension in water and settling for 12 hours at 4 °C) also decreased, as mash pH decreased.

## pH Control During Fermentation

*Correlation of Wort FAN Content and Beer pH*

During fermentation, the composition of the buffer systems present (from wort to beer) change, so that pH always decreases. A major contribution to the wort buffer system is made by the level of the amino acids—aspartate and glutamate—and of polypeptides containing these acids. Since these compounds are included in the analysis of free-$\alpha$-amino nitrogen, it can be anticipated that wort FAN content will correlate with beer pH.

As shown in Fig. 5, data for wort FAN content (corrected to 1040 ° gravity; 10 °P) shows an inverse relationship to beer pH, with a high degree of correlation. These results were obtained from a series of production brews of related beer types.

However, a similar series of data, obtained from production beers from another brewery (using a different yeast strain) showed the exact opposite of the correlation shown in Fig. 5 viz. a direct relationship, with beer pH increasing as wort FAN content increased.

As discussed subsequently, this anomaly arises from increased wort FAN content being related to two, somewhat antagonistic factors, viz. stimulation of yeast growth and increase in buffering capacity.

The following results refer to small-scale, experimental fermentations, designed to quantify these opposing effects.

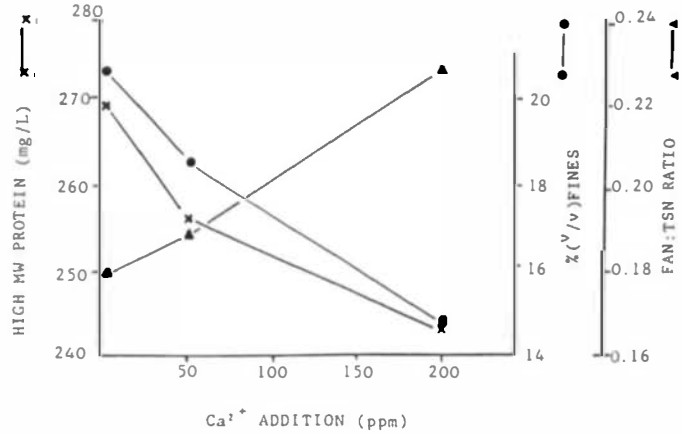


**Fig. 4. Relationship between mash liquor calcium contents and indicators of degree of proteolysis (viz. (A) wort high MW protein content, (B) % (v/v) of fines in spent grains and (C) ratio of wort FAN:TSN levels).**

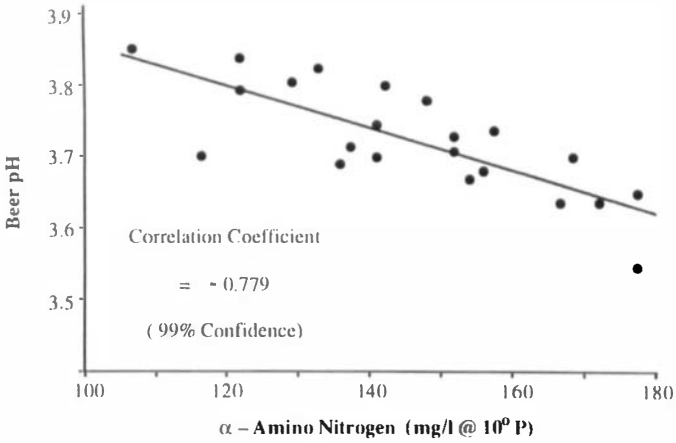


**Fig. 5. Beer pH versus wort FAN content—production brews.**

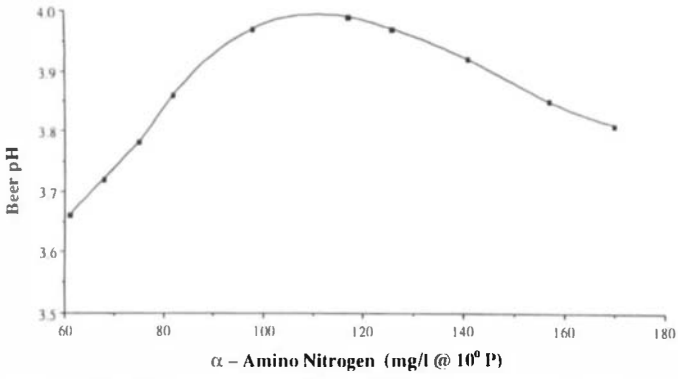


**Fig. 6. Beer pH versus wort FAN content—experimental series.**

*Effect of Yeast Growth on Beer pH*

Factors stimulating yeast growth will lead to increased absorption of amino acids, with increased production of other organic acids and so reduce beer pH. The results obtained from parallel small-scale fermentations of worts of comparable composition, pitched with yeast from a single batch, confirm that:

- increase in wort dissolved oxygen (up to 20 ppm) led to increased yeast growth (as measured by comparing recovered yeast mass at end of fermentation, in relation to yeast mass pitched), and so to reduced beer pH.
- increase in wort zinc content (added up to 0.3 ppm, as zinc sulphate solution) stimulated yeast growth, leading to reduced beer pH.
- increase in wort FAN content led to increased yeast growth and decreased beer pH. This increase in wort FAN was achieved at fixed wort pH by addition of the mixture of serine, leucine and glycine (and so did not alter buffering capacity).

*Effect of Wort Buffering Capacity on Beer pH*

Increasing wort buffering capacity (up to an increase of 50%), by additions of a mixture of aspartate, leucine and glycine, also increased wort FAN content and so led to increased yeast growth; initial wort pH was adjusted to 5.2 in all fermentations.

In this case, as shown in Fig. 6, beer pH increased up to a maximum, from low wort FAN contents and decreased at higher wort FAN contents.

*Effect of Wort Buffering Capacity and Wort pH on Beer pH*

In this fermentation series, increasing additions of the aspartate, leucine, glycine mixture were made (comparable to the procedure above), but the initial wort pH was not corrected, so that the measured wort FAN increase (from 120 to 200 ppm), coupled with increase in buffering capacity (up to 50% increase), caused a decrease in wort pH from 5.2 to 4.5.

In this case, beer pH was maintained virtually constant, at approx. 3.9, although yeast growth increased, relative to increased FAN content.

*Effect of Wort pH on Beer pH*

In this series, wort FAN content was fixed at 150 ppm (at 1040 °) and wort pH decreased in the range 5.2 to 4.5, by addition of dilute sulphuric acid.

This led to decreased beer pH, from 4.0 to 3.7.

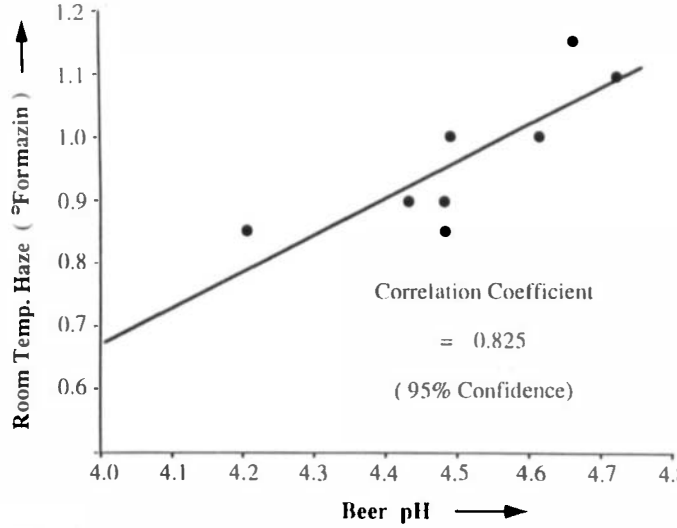


**Fig. 7. Beer pH versus room temperature haze.**

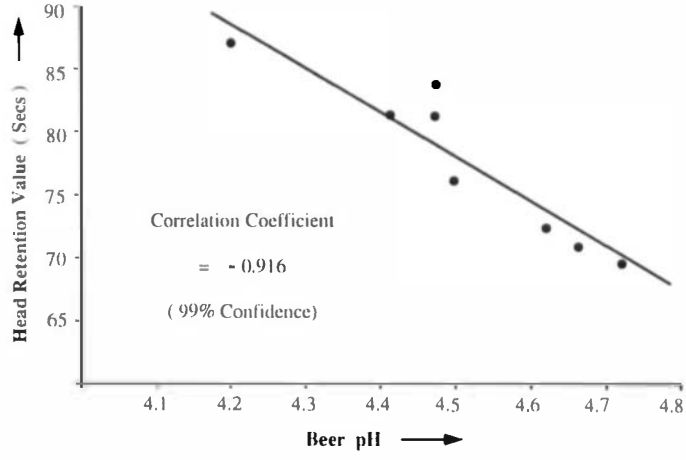


**Fig. 8. Beer pH versus head retention value.**

### Effects of Beer pH Variation on Physical Stability

The results obtained from experiments to alter beer pH at the end of conditioning, prior to filtration, show:

- a direct relationship between beer pH and haze stability, as shown in Fig. 7.
- an inverse relationship between beer pH and head retention value (measured by the Rudin procedure), as presented in Fig. 8.

### Flavor Effects

At low pH values (less than 4.0), beers tend to taste more sharp and acidic, with increased drying after-palate and a ten-

dency for perceived bitterness to be enhanced (even at constant analytical bitterness levels).

Above pH 4.0, the palate effects relate to increased mouth-coating, with enhanced scores for biscuity, toasted characters.

In the experimental flavor series, at very low pH (3.7 and below), the sharp, bitter, drying effects increased in intensity rapidly, with markedly enhanced metallic after-palate.

Above 4.4, the cloying, mouth-coating effects became increasingly more accentuated, with soapy, caustic characters becoming apparent.

## DISCUSSION

### pH Control During Wort Production

The key point for control of pH throughout the brewing process is during mashing. This is due to the major influence that can be exerted at this stage on the content and format of the buffer systems that will operate subsequently in wort and beer.

The grist composition selected for the beer type to be produced, will have the major influence on the constituents present in the wort. The primary proportions of malt to adjunct, the protein content of the malt, the degree of modification and kilning characteristics etc. will all be major determining factors of wort composition.

However, the liquor composition used for mashing and sparging has significant impact on pH control during mashing and wort run-off, and so has a modifying influence on brewhouse performance and the contents of various wort constituents.

The results show that residual alkalinity and calcium ion content in liquor can exert considerably influence on mash and wort pH.

The reactions involved include contributions from the carbonate/bicarbonate buffer system:

$$H_2O + CO_2\uparrow \rightleftharpoons HCO_3^- \rightleftharpoons CO_3^{2-} \xrightarrow{Ca^{2+}} CaCO_3\downarrow$$

and from associations of calcium ions with other buffer systems viz:

(a) $3\,Ca^{2+} + 2\,HPO_4^{2-} \rightarrow 2H^+ + Ca_3(PO_4)2\downarrow$

(b) $Polypeptide - H + Ca^{2+} \rightarrow Polypeptide - Ca\downarrow + 2H^+$

It is questionable, however, whether the phosphate buffer system actually has any great significance in wort/beer pH control, since it has poor buffering action in the pH range 4.0–6.0.

Clearly, there is much merit in reducing liquor alkalinity as low as possible and adding calcium salts to achieve a level of 100–200 ppm during mashing and lautering. The benefit of maintaining a high level of calcium ion during sparging relates to consistent pH control during run-off; thus avoiding excessive extraction of polyphenols and silica, which will be favored as pH rises[4].

The pH value of collected wort is a reflection of pH control during mashing, but it is worth noting that pH at actual mash temperatures is considerably lower (approx. 0.3 units) than pH value determined at 20 °C, due to thermal encouragement of hydrogen ion dissociation. Consequently, selecting the ideal pH for optimal activity of amylolytic and proteolytic enzyme systems is somewhat difficult, especially since conditions applying at mashing bear little resemblance to conditions usually employed for enzymological investigations, i.e., assessment of initial reaction rates, at relatively low temperatures (to avoid excessive thermal denaturation) and at high concentrations of pure substrates.

However, even if optimal pH is difficult to define, reproducible pH condition can be set and judicious control of calcium content allows some measure of control on mash pH. This can be used to exert influence on wort composition and properties. Increase in mash bed permeability is an example and is probably a consequence of the influence of pH and/or calcium ion on the consistency of the gel protein layer on top of the mash bed. The effect on this 3-dimensional matrix of intercross-linked gel protein and polysaccharide (and possibly lipid) complex[5] will be due either to enhanced hydrolysis of these macromolecular structures or to interference of the formation of the cross-linking bonds (including disulphide bonds, hydrogen bonding and hydrophobic interactions) or to both. Oxidation-reduction reactions are also important in this respect. The net effect, as indicated in the result in Fig. 4, is a reduction in the jelly nature of the matrix, so enhancing wort flow through the mash bed.

### pH Control During Fermentation

Control of mash and wort pH has significant influence on the nature and content of the buffering substances in wort.

The effective buffers in wort[6] are carboxylic acid groups, related to:

- Glutamate and Aspartate
- Peptides/Polypeptides containing Glutamate and Aspartate
- Organic acids (e.g., Citrate)

During fermentation, free amino acids are absorbed by yeast, leaving the main buffer system in beer as peptides and polypeptides containing glutamate and aspartate, plus citrate, plus other organic acids (such as lactate, succinate, pyruvate) excreted from yeast. The net effect is that the nature of the buffer system changes, to a lower pH range, but the buffering capacity remains relatively constant.

Since an analysis of wort FAN content will include components of the buffer system, but also will reflect amino acids required for yeast growth, it is apparent why there is not a simple correlation between increasing FAN content and influence on beer pH.

The results obtained demonstrate that the extent with which the net increased acidity production associated with stimulation of yeast growth will impact on beer pH value is dependent on the buffering capacity and wort pH.

Two antagonistic influences arise from an increase in wort FAN content, viz. stimulation of yeast growth causes reduced beer pH, but also increased buffering capacity, leading to increased beer pH. As seen in Fig. 6, the increase buffering capacity effect is more potent at lower FAN contents, with increased acidity production (from higher yeast growth) being the overriding factor at higher FAN contents.

Clearly, the control during mashing of wort composition to achieve consistent FAN content and buffering capacity is very important in this respect and individual circumstances of beer type, grist composition, yeast strain etc., will dictate the desired targets to be achieved routinely.

In fact, adjustment of wort pH has little effect on beer pH, due to the logarithmic nature of the pH scale; a considerable change in wort hydrogen ion concentration is required to exert much impact on beer hydrogen ion concentration (which is approximately 10 times greater). Clearly, this argues against adjusting wort pH at wort boiling stage, for instance, either by acid or calcium salt addition. The control will be considerably more effective during mashing.

Monitoring buffering capacity is a useful tool for routine process control of finished beer pH.

### Effect of Beer pH on Physical Stability and Flavor

The flavor effects of beer pH are well accepted, but will be secondary in importance to the major beer flavor contribu-

tions from raw materials, yeast strain and fermentation conditions.

However, variation in beer pH within a product type can lead to perceived product quality inconsistencies.

The consequence of a late process change in pH towards the end of conditioning can cause considerable disturbance to the stability of the colloidal polypeptide:polyphenol complexes present. The conditions related to the experiments described above are somewhat extreme, but indicate the potential risk to haze stability and head forming ability, if the gravity adjustment liquor, used for high gravity brewing (either pre- or post-filter) has any significant residual alkalinity or calcium content. Clearly, demineralized water has considerable benefit, but at the very least some change in beer pH can be anticipated as a consequence of dilution of the beer buffers, if buffering capacity is not sufficient.

## CONCLUSIONS

The key to consistent beer pH is the maintenance of consistent wort composition and fermentation conditions.

However, pH specifications and tolerable ranges should take cognizance of the logarithmic nature of pH and try to reflect the relevance of tight control of the actual hydrogen ion concentration.

The nature of the buffer systems in wort and beer that will dictate pH control throughout the brewing process is established during mashing and this stage represents the key process control point.

For a given grist composition, mash pH may reflect any potential variations in raw material supplies, so that additional control of mashing conditions can be obtained by maintaining a consistent calcium level, either (and more ideally) in both mashing and sparging liquors or by addition of calcium salts at mashing-in.

## ACKNOWLEDGEMENT

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