Journal of Microbiology,
Biotechnology and
Food Sciences

Tóth et al. 2013 : 2 (Special issue 1) 2043-2051

REGULAR ARTICLE

WATER HARDNESS AS AN IMPORTANT PARAMETER OF PH

Žigmund Tóth, Helena Frančáková, Miriam Solgajová, Štefan Dráb*

Address: Ing. Žigmund Tóth PhD.

Slovak University of Agriculture, Faculty of Biotechnology and Food Sciences, Department of Storing and Plant Products Processing, Tr. A .Hlinku 2, 949 01, Nitra, Slovakia, phone number: 037 654 4421.

*Corresponding author: zigmund.toth@uniag.sk

ABSTRACT

Quality of final product is to great extent influenced by intermediate products that are formed during beer production. In addition quality of pH is one of the most important properties that forms suitable medium for activity of enzymes complexes that have crucial influence on character of produced wort. Moreover enzymes influence the yield of production process and quality of final product as well. Quality of boiling water and especially its hardness have crucial task in terms of keeping optimal qualitative parameters. Water hardness is given by amount of salts, mainly calcium and magnesium salts. It is expressed as absolute hardness which is given by sum of temporary (carbonate) and permanent (noncarbonate) hardness. In our work we solved the effect of total water hardness on final pH of various intermediate products. We used different water samples and we prepared variants of total hardness by stirring of unpurified water with distilled water thus we achieved various values of hardness. For comparison we prepared several brews with regard to combinations of unpurified water and distilled water. Higher pH of boiling water was caused due to higher water alkalinity that negatively affected enzyme complex present in used malt. Presence of hydrogenphosphates in used malt had high buffering ability and pH lowering ability. Such unfavorable result could be adjust by use of various additions of acidulates that would have in great extent influence on beer final price therefore boiling water adjustment seems to be the most acceptable approach.

Keywords: water hardness, pH, mash, fisrt wort, wort, hopped wort, beer

INTRODUCTION

According to **Basařová *et al.* (2010),** amount of dissolved salts in water is a very important criteria used in practice for assessing the suitability of water for specific technological applications. In the past, the most used term for dissolved salts was the term "hardness", which is still commonly used in practice. It was either the sum of calcium, magnesium and barium ions, but also it was the amount of all cations with charge number greater than 1.

Poláček *et al.* (2010) states that it is more correct to express the content of calcium and magnesium separately and not as its sum by using the term hardness, as their chemical, technological or biological properties are not the same. However, despite the objections of many chemists around the world the concept of hardness persists throughout the world, as it is a term used in the public and professional practice.

According to **Šrogl (2000)** in terms of hardness it is recognized: soft water: <1.3 $mmol.dm^{-3}$, moderately hard water: from 1.3 to 2.5 $mmol.dm^{-3}$, hard water: from 2.5 to 3.8 $mmol.dm^{-3}$, very hard water: >3.8 mmol.dm-3.

Water for production of world-famous Pilsner type beer should be very soft with a predominance of carbonate hardness of 0.23 $mmol.dm^{-3}$. Such water is used to produce light, medium-fermented beers and bitter beers with a full taste (**Basařová *et al.*, 2011**). During wort boiling with hops, hydrogen carbonates of alkalic metals alter by splitting off carbon dioxide to more or less soluble carbonates and this affects calcium-carbonate balance (**Lewis *et al.*, 2002**).

Magnesium carbonate is a volatile, during prolonged boiling it breaks down and can be completely removed out of solution. Non-carbonate water hardness is formed by calcium and magnesium salts of sulphuric acid, hydrochloric acid, nitric acid, and others, that do not change during a boiling. Total and temporary hardness are determined analytically and permanent hardness is calculated from their difference (**Basařová *et al.*, 2011**).

Boiling water pH should be between 6.8 to 7.0. As the pH of drinking water ranges from 6.0 to 8.0 it should be for the boiling process adjusted. The pH formation of the mash during the boiling is greatly affected by salts of boiling water. Generally, Ca^{2+} and Mg^{2+} are responsible for the reduction of pH and hydrogen carbonate ions for its increase. Hydrogen carbonate anions in the reactions running at high temperatures utilize hydrogen cations, reduce acidity and release carbon dioxide. The acid reaction of mash during boiling process ensure dissociated dihydrogen phosphates ($H_2PO_4^-$), hydrogen phosphates (HPO_4^{2-}) and phosphates (PO_4^-) of malt. The first phosphates show acid reaction, the second weakly alkalic reaction and the third alkalic reaction.

According to **Basařová *et al.* (2010)** calcium cations may be present in water at high concentrations (up to 200 $mg.dm^{-3}$), they stimulates the activity of certain malt enzymes, especially those that support the stability of the α-amylase by its protection against thermal denaturation, but they also promote the activity of endopeptidases.

Bamforth (2003) also claims that calcium promotes α-amylase activity, which then reacts with phosphates in malt, which leads to a reduction of pH to an appropriate level for boiling. **Polacek *et al.* (2010)** adds that calcium promotes protein coagulation, it stimulates the activity of the yeast and support their flocculation.

Magnesium cations mostly come from malt and only about one third is from the boiling water. They are more soluble than calcium ones and less affect the pH as calcium cations. Magnesium stimulates the activity of the fermentation enzymes (**Šrogl, 2000**), (**Kunze, 2004**). Author states that the magnesium takes part at stabilization of pH in wort and hopped wort, but he argues that although magnesium cations have a positive effect on the activity of certain enzymes, its content higher than 0.125 $mmol.dm^{-3}$ is considered to be harmful.

Sulphate anions SO_4^{2-} are during fermentation source of carbon dioxide which as a natural antioxidant has positive effect in sensorial and colloid stability of beer, but it is also a substrate for the production of hydrosulphide. Calcium and magnesium sulphates increase in reaction with phosphates acidity of mash and wort (**Basařová *et al.,* 2010**), (**Ahrens *et al.,* 2003**) .

Chloride anions Cl^- promote activity of malt amylases but activity of peptidases they do not affect. They also inhibit yeast flocculation. Magnesium chlorides have such a negative effect as magnesium sulphates (**Šrogl, 2000**),(**Narziss, 1985)**.

Nitrates NO_3^- may be present in beer, as well as in drinking water mostly up to 50 $mg.dm^{-3}$ states **Basařová *et al.* (2010)**. Nitrates concentration in the boiling water affects the concentration of nitrates in beer (**Cvengroschová, Šmogrovičová, 2007**).

The objective of our study was to solve the effect of total water hardness on final pH of various intermediate products.

MATERIAL AND METHODS

Sample preparation

Samples were prepared in mini brewery of SPU. For each beer brew we used 36 litres of water and 12 kg of malt grit. Volume of used water was adjusted in various rates of unpurified and distilled water. From such prepared water we carried out analyses of total hardness by complexometric titration by use of complexone 3. Preparation of solutions and whole assessment was carried out according to analytical methods of **Kučerová (1990).**

Measurement

Determination and calculation of water hardness

Total water hardness was determined by titration method by use of complexone 3. In alkaline medium with pH 10, forms complexone 3 chelates, at first with calcium and than with magnesium ions. End of titration e.g. extinction of free magnesium ions is indicated by coloured change of indicator. Usage of complexone solution is proportional to concentration of calcium and magnesium ions in water (water hardness).

Total concentration of calcium and magnesium ions is calculated:

$$C\ (Ca + Mg) = \frac{a.\ 0.05.\ 1000}{V}$$

Where: c (Ca + Mg) – is total concentration of calcium and magnesium in $mmol.dm^{-3}$

a – usage of complexone 3 solution with concentration c (CH3) = 0.05 $mmol.dm^{-3}$

V – volume of sample in cm^3

Determination of pH

pH was determined by potentiometry by use of glass indication and calomel comparative electrode using pH meter WTW inoLab® pH Level 2, with set up “ready to go”. For determination sample of 100 cm^3 of mash, first wort, wort, hopped wort, wort after fermentation and prepared beer was used.

RESULTS AND DISCUSSION

Table 1 The water hardness of individual brews determined by complexone 3

Number of brew	Water sample 100 cm³	Usage of complexone 3 cm³	Water hardness mmol.dm^{-3}
1.	Unpurified water	6.4	3.2
2.	(3:1)	4.8	2.4
3.	(2:1)	4.2	2.1
4.	(1:1)	3.2	1.6
5.	(1:2)	2.2	1.1
6.	(1:3)	1.6	0.8
7.	Distilled water	0.2	0.1

Table 1 presents proportions of distilled and unpurified water. Unpurified water showed very high hardness 3.2 mmol.dm^{-3}. Such values are not recommended for light beers boiling, this water is rather suitable for dark special beer boiling, states **Basařová *et al.* (2011).** According to results in table 1 we could see that values achieved by mixture of unpurified and distilled water were not proportional to their amounts but they deviate in minimal values. This could be caused by various temperatures during the time of samples stirring because distilled water had room temperature while unpurified water was taken from rural water pipe and had temperature 12 to 15°C.

Table 2 The pH of intermediate products and final product in dependence on water hardness

Water hardness mmol.dm^{-3}	pH of mash	pH of first wort	pH of wort	pH of hopped wort	pH of wort after primary fermentation	pH of final product
3.2	6.15	5.95	5.85	5.83	4.88	4.81
2.4	6.12	5.92	5.85	5.83	4.81	4.78
2.1	6.10	5.92	5.83	5.80	4.76	4.72
1.6	6.10	5.90	5.80	5.78	4.75	4.70
1.1	5.90	5.85	5.75	5.70	4.66	4.55
0.8	5.70	5.68	5.62	5.60	4.58	4.52
0.1	5.60	5.58	5.50	5.40	4.51	4.42

Table 2 presents comparison of total hardness with pH values of intermediate products and final product. Higher value of total hardness from 2.1 to 3.2 mmol.dm^{-3} kept higher pH values of mash (6.10 - 6.15), pH of first wort (5.92 - 5.95), pH of wort (5.83 - 5.85) and pH of hopped wort (5.80 - 5.83). These values are absolutely inconvenient to standard during technological process of wort preparation where there is recommended to keep values of pH in terms of 5.2 – 5.3. In this condition comes to formation of tan stuffs and protein complexes and moreover it comes to its precipitation, which lead to ideal clarification of wort (**Šrogl, 2000**). To improve pH in case of using such boiling water we could acidify wort mainly by lactic acid or by sulphuric acid, states **Basařová *et al.* (2010).** Brews prepared from unpurified water by its improvement with distilled water to reach lower values (form 0.8 to 1.6 mmol.dm^{-3}), helped to lower the values of wort pH, but still remain on quite high values (from 5.6 do 5.78). In case of these brews, it came to better interaction of proteins and tan stuffs that led to better technological parameters. These parameters showed up mainly during process of primary fermentation, secondary fermentation and they reflected in better qualitative parameters of final product. The most optimal, should be from the water hardness point of view, the hardness of distilled water with parameter 0.1 mmol.dm^{-3}, which was proved with regard to pH values. In sensorial test these samples were evaluated as samples with low sharpness and fullness, which means serious problem for quality of produced beer.

For this reason we would incline to the opinion according to **Kunze (2007),** that for light beer boiling it should by used just soft water but in certain proportion of carbon and non carbon hardness. This idea is also confirmed by **Basařová *et al.* (2011),** who characterize classical light beer of pilsner type as a beer with carbon hardness of 0.23 $mmol.dm^{-3}$. According to **Chládek (2007),** beside total water hardness very important is proportion of carbon and non carbon hardness that should be in the rate of 1:1 or 2:1, in favor of carbon hardness.

CONCLUSION

Focus of our work was to monitor utilization of boiling water for beer production in mini brewery of SPU. Parameter of water hardness was selected as an important parameter and subsequently analyses of pH of intermediate products were carried out. These products were formed during the process of beer boiling and in other technological phases. Preparation of various proportions of boiling water was assured by stirring boiling water with distilled water. Total water hardness, has in term of calcium and magnesium salts, great influence on final character of prepared intermediate products during the period of beer boiling. It was manifested in changes of physical-chemical properties, such as pH that we have evaluated in our work. For individual brews we choosed different values of total hardness. We also choosed unpurified water and in one brew we used distilled water, both without treatment. The best values of wort pH during the boiling process were achieved by use of distilled water in comparison with values declared in practice. However, final product did not show sufficient qualitative values during sensorial evaluation. For that reason the best samples of beer were samples prepared with water of hardness 1.1 to 1.6 $mmol.dm^{-3}$. In conclusion it would be more ideal in future to prepare boiling water not as a mixture of unpurified and distilled water but to lower the water hardness by various methods such as by use of decarbonization with lime milk or by use of ionites. By this procedure we could prepare boiling water that would be qualitative guarantee of better prepared wort and subsequently assumption for product with excellent quality. We have to keep in mind other factors that could affect technological process, such as quality of brewing yeast, time of keeping fermentation process and hygienic and sanitation arrangements as well. Boiling water and especially its hardness is an important parameter that has influence on achieving optimal values of pH of intermediate products obtained by beer production as well as final product.

Acknowledgments: This work has been supported by KEGA project (KEGA 015/SPU-4/2011).

REFERENCES

AHRENS, A. SCHILDBACH, S. 2003. Water as raw material in breweries and malthouses. European Brewery Convetion, 29 th Congress, Dublin, Nürnberg Fachverlag Hans Carl 2003. 150 - 155 p., ISBN 90-70143-22-4

BAMFORTH, CH. 2003.: Beer Tap Into the Art and Science of Brewing.2nd.ed.,New York, Oxford University Press, 2003. 256 p. ISBN 0-19-515479-7

BASAŘOVÁ, G. – ŠAVEL, J. – BASAŘ, P. – LEJSEK, T. 2010. Pivovarství : Teorie a praxe výroby piva. Praha : Vysoká škola chemicko-technologická, 2010. 904 s. ISBN 978-80-7080-734-7

BASAŘOVÁ, G. – HLAVÁČEK, I. – BASAŘ, P. – HLAVÁČEK, J. 2011. České pivo. Třetí doplněné vydání., Praha: HBT, 2011. 394 s. ISBN 978-80-87109-25-0

CVENGROSCHOVÁ, M. – ŠMOGROVIČOVÁ, D. 2007. Chmeľové preparáty a faktory ovplyvňujúce priebeh chmeľovaru. In *Chemické listy,* roč. 101, 2007, č.4, s. 287 – 291

FANTOZZI, P. – MONTANARI, F. – MANCINI, F. – GASBARRINI, A. – ADDOLORATO, G. – SIMONCINI, M. – NARDINI, M. – GHISELLI, A. – SCACCINI, C. 1998. In vitro antioxidant capacity from wort to beer. Lebensmittel, Wisserschaft, 1998, n. 31, p. 221 - 227

CHLÁDEK, L. 2007. Pivovarnictví. 2 vyd., Praha : Grada Publishing, 2007. 208 s. ISBN 978-80-247-1616-9

KUČEROVÁ, J. 1990. Chemické kontrolné metódy pre 4.ročník stredných priemyselných škôl potravinárskych študijného odboru kvasná technológia. Bratislava: Alfa, 1990. 384 s. ISBN 80-5-00619-5

KUNZE, W. 2007. Technologie Brauer und Mälzer. 9. Auflage, Berlin: VLB- Versuchs- und Lehranstalt für Brauerei, 1999. 1118 s. ISBN 978-3-921690-56-7

KUNZE, W. 2004. Technology Brewing and Malting. 3 rd International Ed ., Berlin: Verlagsabteilung VLB, 2004. 939 p. ISBN 3 – 921690 – 34 - X

LEWIS, M. J. 2002 - YOUNG, T. W. Brewing. Kluwer Academic/Plenum Publishers, 2002, 398 p., ISBN 0-306-47274-0.

MOLL, M. 1994. Beer & Coolers, Andver, Hampshire, Intercept Ltd., 1994. 495 p. ISBN 1 – 898298 – 2

NARZISS, L. 1985. Die Bierbrauerei, Vol 2 : Die Technologie der Würzbereitung, 6. Auflage. Stuttgart: F. Enke Verlag, 1985. 385 p. ISBN 3 – 432 – 85006 - 9

POLÁČEK, Š. –BULLA, J. – FRANČÁKOVÁ, H. 2010. Voda, úprava a použitie vo výžive ľudí. Nitra: Vydavateľstvo SPU, 2010. 136 s. ISBN 978-80-552-0272-3

ŠROGL, J. 2000. Varní voda. In *Technologie výroby sladu a piva.* Praha: Výskumný ústav pivovarský a sladařský, 2000. s. 140 – 152. ISBN 80-902658-6-3