Do brewers need a starch modification index?

HARTONG INDEX AT 45 °C (VZ 45 °C) AS A QUALITY CRITERION | This contribution is a review of scientific investigations of the Hartong Index at 45 °C (VZ 45 °C) and a discussion of the respective findings. In a previous publication, the authors subdivided issues arising into three major breakdown processes i.e. proteolysis, cytolysis and amylolysis in the malting and brewing process [16]. This article summarises the outcome of the investigations and critically discusses the question whether VZ 45 °C is a useful specification for assessing malt quality.

SINCE VZ 45 °C has been developed between the 1930's and 1950's by *Hartong* and *Kretschmer* [15], it has become a widely accepted specification for assessing quality of barley malt. In brewing technology, an excessive difference especially between the Kolbach index and VZ 45 °C is regarded as a quality defect [1]. Despite the fact that this index is taken very seriously, its information value is controversial and remains in doubt.

In recent times, new breeds of barley varieties such as Annabell and Pasadena have become available. These give rise to malt with a low VZ 45 °C though good brewing quality results. The sensory tests in the context of the Berliner Programm led to excellent results, and the beers scored comparatively well in the staling test ([2],[3]).

Against the backdrop of the currently widespread infusion mashing with high mashing-in temperatures, the question arises whether VZ 45 °C is still a suitable criterion for assessing quality of malt for use in brewing.

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Historical background and technological position

In the 1930's, VZ 45 °C was developed as part of a process for determining modification properties of malt in the laboratory of Hartong [11]. He selected four temperature stages (25 °C, 45 °C, 65 °C and 85 °C) for mashing isothermally for one hour. The 25 °C mash was to provide information about previously modified extract and the activity of the phytase (a phosphate esterase), the 45 °C mash assessed proteolytic activities, the 65 °C mash measured the activity of all enzymes and the 85 °C mash covered extract modification as a consequence of starch gelatinisation. The four indices were averaged, 60 was deducted, and they were defined as modification index. Table 1 shows an assessment of the modification index according to Hartong.

A major drawback of this method was the large amount of time involved [17]. There was consensus that the carbohydrates were the key to the modification index and that the modification process during mashing was influenced by the totality of enzymes present in the malt and the degree to which the substrate could be attacked, whereby – in this case – the propensity to attack was equated to malt modification [12]. Hartong [13] was furthermore of the opinion that the modification index or the individual relative extract indices provided a possibility of assessing brewing quality and also of pinpointing the causes of potential malt deficiencies.

In 1939, Hartong [14] regarded VZ 45 °C as an index for the enzyme potential of barley. In 1953, Hartong and Kretschmer [15] modified the analysis method. 25 °C was replaced by 20 °C, and the 85 °C mash was replaced by the 80 °C mash. In addition to the Hartong Index, the various individual indices are also taken into account. Special significance is accorded to VZ 45 °C as it assesses both production as well as enzymatic power of malt. It closed a gap in malt analysis. 36 per cent was quoted as standard. If VZ 45 °C is below the standard, the malt has been weakened enzymatically due to improper treatment. This affects proteolytic enzymes in particular. As of that time, the fine-coarse difference, the cold extract index, the longitudinal section and VZ 45 °C were sufficient to describe malt ad-

ASSESSMENT OF THE MODIFICATION INDEX IN ACCORDANCE WITH HARTONG

Hartong Index	Malt assessment
0 - 3.5	decreasing undermodification
4 - 4.5	standard modification for draught beers
5	ideal modification
5.5 - 6	appropriate modification for bottled beers
6.5 - 10	increasing overmodification

Table 1

COEFFICIENTS OF CORRELATION (R) OF VZ 45 °C AND VARIOUS QUALITY CHARACTERISTICS OF BEER AND WORT

	Wort analyses			Beer analyses		
n = 36	total nitrogen	high molecular weight nitrogen	FAN	Foam (NIBEM)	Filterability (G_{max})	Viscosity
r	[mg/100 ml]	[mg/100 ml]	[mg/100 ml]	[s]	[g]	[mPa × s]
VZ 45 °C	0.08	-0.08	-0.02	0.01	0.23	0.14

Tale 2

equately. The Hartong methods of analysis were simply meant to put assessment on a more solid footing. This index is nowadays known as the "modification index according to Hartong" or as "Hartong Index" (HI). According to Hartong and Kretschmer, VZ 45 °C values and VZ 25 °C values below the standard values of 36 per cent or 25 per cent may cause problems during lautering, fermentation, clarification, filtration and shelf life. This is attributed to weakened activity of proteolytic enzymes resulting from improper kilning.

Piratzky [22] was of the opinion that the HI is influenced by the modification of grain structure to a limited extent but that it still provides a suitable measure of enzymatic activity. He regarded VZ 45 °C in particular as the most informative index. *Scriban* [24] concluded from his investigations in 1963 that extract at 45 °C and pH value of the same wort provide comprehensive information on the malt, the α-amylase content being described particularly well. This is contradicted by Kretschmer [18] who assessed α-amylase activity on the basis of VZ 80 °C.

In 1967, Kretschmer [18] established a correlation between an inadequate VZ45 °C and poor yeast propagation that in turn has a negative influence on clarification, aroma and shelf life. He quoted a limit value of at least 36 per cent for VZ 45 °C and values over 40 per cent for good colloidal stability of a beer.

Based on investigations by *Lie* and *Rasch* [19], VZ 45 °C correlates with the FAN content of wort. According to the findings of *Bellmer* [7], a VZ 45 °C of 38 to 40 per cent guarantees that yeast is adequately supplied with assimilable nitrogen.

In summary, it can be said that all authors are of the opinion that VZ 45 °C provides information on malt modification. In brewing science, modification processes are understood as referring both to physical as well as enzymatic modification. Accordingly, these processes are influenced by enzymatic activities, physical parameters (e.g. temperature) as well as by properties of the substrate as such. Indices describing a modification process always encompass several factors.

If VZ 45 °C is a measure of proteolysis, there has to be a relationship between VZ 45 °C and one of the proteolytic indices of malt or a wort or beer quality characteristic.

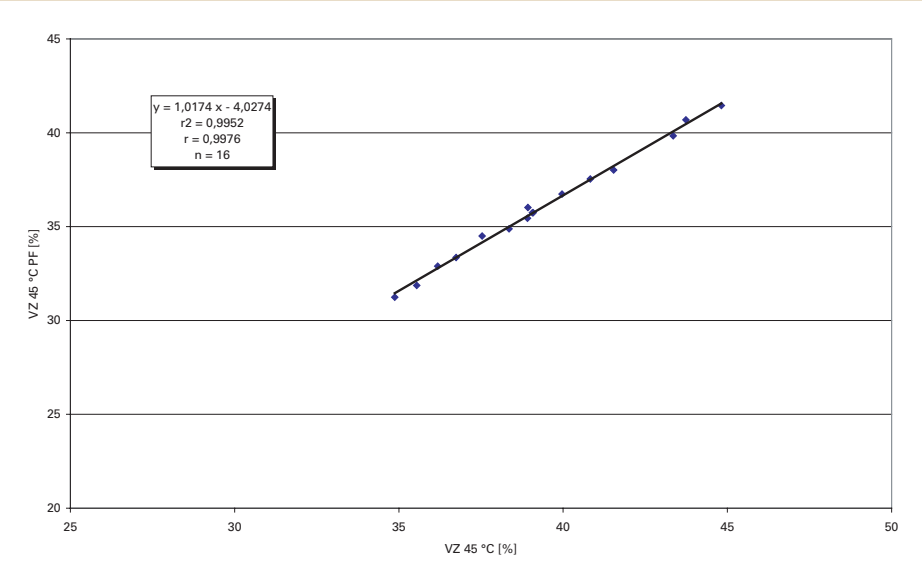

Fig. 1 Correlation between VZ 45 °C and VZ 45 °C PF

If VZ 45 °C is a cytolytic parameter, it has to correlate with an index measuring cytolysis. If this is not the case, there has to be a relationship with a wort or beer quality characteristic that describes cytolysis. Otherwise, VZ 45 °C cannot be regarded as a cytolytic index.

If VZ 45 °C is an amylolytic parameter, it has to correlate with an amylolytic activity, a parameter describing the product or the substrate. α-amylase and β-amylase are the most important amylolytic activities. Fermentable sugars and dextrins are product parameters. The physical properties of starch are understood to be substrate parameters.

Physical properties of barley starch

Starch is the main component of barley, accounting for 55 to 65 per cent of dry matter. It is present in the form of large (A-type, 10-25 µm) and small (B-type, 1-5 µm) starch granules. Standard barley starch is composed of 20-30 per cent amylose and 70-80 per cent amylopectin. Gelatinisation temperature for barley starch is 61-62 °C, small granules gelatinise only at 75-80 °C [21]. The structure in particular, i.e. the chain length, as well as the degree of branching of amylopectin is responsible for physical properties and thus for gelatinisation temperature. Depending on the measuring principle used, gelatinisation temperature may vary by some degrees [23].

Amylolysis during malting and mashing

Germination during mashing takes place predominantly below gelatinisation temperature so that starch is hydrolysed enzymatically very slowly ([8],[20],[21]). During kilning, temperatures above gelatinisation temperature arise. In the case of pale malt, with water content in the grain less than 20 per cent [20], starch can no longer be gelatinised. During mashing in the brewhouse, starch that has been attacked enzy-

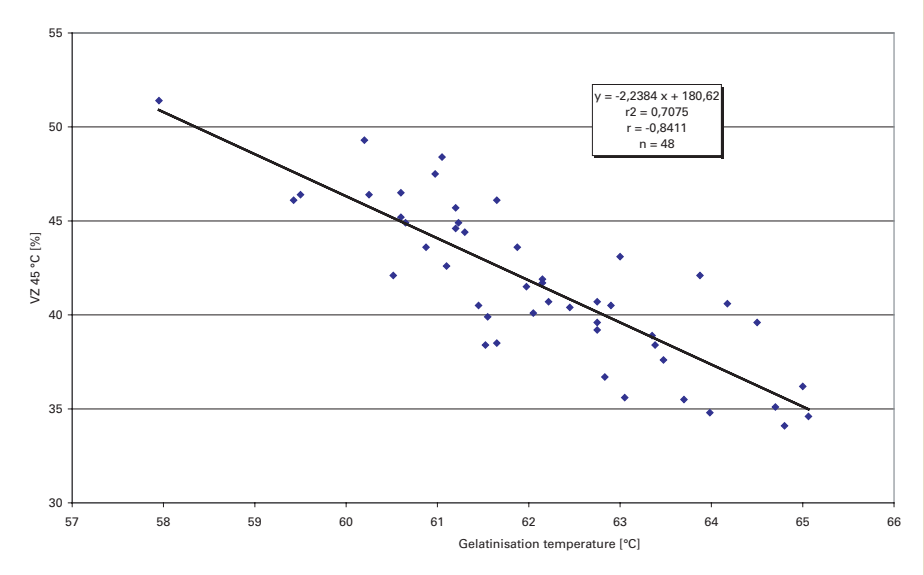

Fig. 2 Gelatinisation temperature plotted against VZ 45 °C

matically during germination or injured during milling is mainly hydrolysed up until reaching gelatinisation temperature ([9], [10], [21], [25]). Investigations have shown that, in the congress mashing process, only a small quantity of high molecular weight starch is present after reaching the 70 °C rest ([8],[20]). In view of the partly very high gelatinisation temperatures, small starch granules are partly not broken down and get into the wort [21].

Results

The results presented here are a summary of the studies on VZ 45 °C published by *Keßler* et al. [16]. The material and methods used have also been described in these investigations.

Is VZ 45 °C an index of proteolysis?

VZ 45 °C does not correlate with any proteolytic index (FAN of congress wort, soluble nitrogen, degree of protein modification). Moreover, there is no relationship between VZ 45 °C and the quality characteristics of wort and beer shown in Table 2, based on the investigations of the Malting Barley Association [2] in the context of the Berliner Programm. In order to address the issue as to whether VZ 45 °C is a proteolytic parameter, one can look at the influence of modified protein on calculation of VZ 45 °C. VZ 45 °C is the ratio between the extract of the sample mashed at 45 °C and the extract of the congress wort. If protein content is deducted from the two samples, the protein-free extract will result. The ratio formed from same is VZ 45 °C protein-free (VZ 45 °C PF). VZ 45 °C PF has a highly significant correlation (r = 0.9976; n = 16) with VZ 45 °C (see Fig. 1). Though the modified protein has an influence on the absolute value of VZ 45 °C, it does not alter anything regarding the relationship of individual samples one to another.

Is VZ 45 °C an index of cytolysis?

VZ 45 °C does not correlate with any cytolytic index of malt. The question whether VZ 45 °C is an index of cytolysis can be answered without any doubt by looking at the Annabell variety. It has a relatively low VZ 45 °C but has good cytolytic properties. This has been repeatedly confirmed in the annual investigations on variety approval carried out by the German Varieties Authority ([4],[5]). The Annabell variety has above-average filterability despite a low VZ 45 °C (see [16]). It can thus be concluded that VZ 45 °C is not an index of cytolysis.

VZ 45 °C is an index of amylolysis

91 per cent of components dissolved in 12 ° wort are carbohydrates, 6 per cent are proteins. The remaining 3 per cent are made up of minerals and a multiplicity of other substances. 99.5 per cent of carbohydrates are starch breakdown products [21]. When ignoring modified protein and the other components, VZ 45 °C describes the ratio between starch breakdown products of the isothermal 45 °C wort and starch breakdown products of congress wort. Accordingly, VZ 45 °C should be an index of amylolysis. Being an index of amylolysis, VZ 45 °C should describe either the amylolytic enzymes, the products of amylolysis or the educt of amylolysis.

Investigations have shown that there is no significant correlation between VZ 45 °C and the amylolytic activities of α-amylase (r = 0.2961; n = 48) and diastatic power (r = 0.1493; n = 48). Final attenuation (r = 0.2666; n = 48) and extract (r = 0.2170; n = 48) can serve as indices describing the product of amylolysis. Both do not correlate with VZ 45 °C. As VZ 45 °C does not correlate with either the amylolytic enzymes or with the products of amylolysis, there has to be a correlation with starch.

Native starch is hydrolysed enzymatically very slowly below gelatinisation temperature ([10],[25],[26]). Gelatinisation temperatures of samples tested range between 57.6 and 65.1 °C and thus clearly above 45 °C. Thus, starch modified during the 45 °C mash comprises starch granules which have been pre-modified enzymatically during malting or damaged during milling.

When assuming that VZ 45 °C describes the portion of starch that can be attacked enzymatically, the question arises whether there is a relationship with the degree of modification of cell walls. When taking the model of cell wall structure of the endosperm according to *Bamforth* [6], cytolysis precedes amylolysis. Samples with a low VZ 45 °C could thus be undermodified cytolytically. As mentioned, this contradicts what has been found to apply to the Annabell variety. Starch of barley malt samples with a high VZ 45 °C can be attacked enzymatically more readily than that of samples with a low VZ 45 °C. Reduced susceptibility to attack starch granules does not correlate with higher amylolytic activity, this is in line with the findings of *Slack* and *Wainwright* [25].

Based on the 48 samples tested (6 varieties from 8 locations), a relationship between gelatinisation temperature and VZ 45 °C may be suggested (Fig. 2). With a coefficient of correlation of r = –0.8411, there is a highly significant correlation. This correlation confirms the thesis that VZ 45 °C is an amylolytic index. But it is unlikely that VZ 45 °C is solely determined by gelatinisation temperature.

Discussion

The results indicate that VZ 45 °C is an amylolytic index as it is the ratio of starch

modifiable at 45 °C and starch modifiable in the congress mashing process. So to speak, VZ 45 °C represents the starch modification index. The question that then arises is whether the starch modification index provides valuable information for the brewing process and is thus an important index when purchasing malt.

It is possible to a limited degree only to use VZ 45 °C as an indicator of quality defects of a batch as this would be expedient only when the variety involved is known and when the batch is varietally pure. Barley with a variety-specific high VZ 45 °C or with a narrow margin to the Kolbach index can definitely not be processed into malt with a deficit showing solely in VZ 45 °C or where VZ 45 °C has an offset from the Kolbach index, without the remaining specifications also indicating quality shortcomings.

Is a low VZ 45 °C invariably a quality deficit? The higher the degree of modification, the higher the portion of readily hydrolysable starch below gelatinisation temperature. In the case of beers carrying the objective of being produced with a high attenuation, a high degree of modification is definitely advantageous unless this has been brought about by excessive malting, invariably leading to higher losses.

There is no basis for the argument often put forward that malts with a low VZ 45 °C result in inferior foam and give rise to filtration difficulties. The values obtained with the Annabell variety in the context of the Berliner Programm clearly show that excellent worts and beers can be produced from malt with a low VZ 45 °C, without causing problems during fermentation or filtration. A variety such as Annabell has a low attenuation, this can be attributed to the fact that this variety has low amylolytic activities [4] which in turn have no correlation with VZ 45 °C. It can thus be concluded that VZ 45 °C does not represent an important index for assessing malt quality.

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References

1. Arbeitsgemeinschaft zur Förderung des Qualitätsgerstenanbaues im Bundesgebiet e. V. (edt.): Braugersten Jahrbuch. 38th edition. Eichenau, 2000.
2. Arbeitsgemeinschaft zur Förderung des Qualitätsgerstenanbaues im Bundesgebiet e. V. (edt.): Braugersten Jahrbuch. 39th edition. Eichenau, 2001.
3. Arbeitsgemeinschaft zur Förderung des Qualitätsgerstenanbaues im Bundesgebiet e. V. (edt.): Braugersten Jahrbuch. 40th edition. Eichenau, 2002.
4. Arbeitsgemeinschaft zur Förderung des Qualitätsgerstenanbaues im Bundesgebiet e. V. (edt.): Braugersten Jahrbuch. 41st edition. Eichenau, 2003.
5. Arbeitsgemeinschaft zur Förderung des Qualitätsgerstenanbaues im Bundesgebiet e. V. (edt.): Braugersten Jahrbuch. 42nd edition. Eichenau, 2004.
6. Bamforth, C. W.; Kanauchi, M.: A Simple Model for the Cell Wall of the Starchy Endosperm in Barley. In: Journal of the Institute of Brewing 107 (2001), No. 4, pp235 – 240.
7. Bellmer, H. G.: The Importance of Barley and Malt, Used in the Production of Beer, according to the "German Law of Purity in the Production of Beer" (German Reinheitsgebot). In: European Brewery Convention: Barley and Malting Symposium. Zeist, 1975, pp41 – 55.
8. Bertoft, E.; Henriksnas, H.: Starch Hydrolysis in Malting and Mashing. In: Journal of the Institute of Brewing 89 (1983), No. 4, pp279 – 282.
9. Bertoft, E.; Kulp, S. E.: A Gel-Filtration Study on the Action of Barley Alpha-Amylase Isoenzymes on Granular Starch. In: Journal of the Institute of Brewing 92 (1986), No. 1, pp69 – 72.
10. Gibson, T. S.; Alqalla, H.; McCleary, B. V.: An Improved Enzymatic Method for the Measurement of Starch Damage in Wheat-Flour. In: Journal of Cereal Science 15 (1992), No. 1, pp15 – 27.
11. Hartong, B. D.: Der Lösungsgrad des Malzes. In: Wochenschrift für Brauerei 53 (1936), Nr. 11, S. 81 – 83.
12. Hartong, B. D.: Der Lösungsgrad des Malzes III. In: Wochenschrift für Brauerei 55 (1938), No. 1, pp5 – 8.
13. Hartong, B. D.: Die Brauqualität des Malzes, ihre Bestimmung und ihre Bedeutung für die Bierbereitung. In: Wochenschrift für Brauerei 55 (1938), No. 49, pp385 – 389.
14. Hartong, B. D.: Zusammenhänge zwischen Mälzungsbedingungen und Malzgüte. In: Wochenschrift für Brauerei 56 (1939), No. 44, pp317 – 320.
15. Hartong, B. D.; Kretschmer, K. F.: Ein Beitrag zur analytischen Ermittlung des Malzbrauwertes. In: Monatsschrift für Brauerei (scientific supplement) 6 (1953), No. 10, pp109 – 117.
16. Keßler, M.; Kreisz, S.; Zarnkow, M.; Back, W.: Investigations about the relative Hartong Extract at 45 °C. In: Monatsschrift für Brauwissenschaft 58 (2005), No. 4, pp56 – 62.
17. Kolbach, P.: Die Beurteilung von Darrmalz. In: Wochenschrift für Brauerei 55 (1938), No. 1, pp1 – 5.
18. Kretschmer, K. F.: Über die Güteeigenschaften von Braumalzen. In: Brauwelt 107 (1967), No. 48/49, pp929 – 935.
19. Lie, S.; Rasch, S.: Proline in Wort in Relation to Analytical Data of the Used Malt. In: European Brewery Convention (edt.): European Brewery Convention Congress. Interlaken, 1969, pp 193 – 203.
20. Narziss, L.: Die Bierbrauerei – Die Technologie der Malzbereitung. 7th edition. Stuttgart: Ferdinand Enke Verlag, 1999.
21. Palmer, G. H.: Cereals in Malting and Brewing. In: Palmer, G. H.: Cereal Science and Technology. Aberdeen: Aberdeen University Press, 1989, pp61 – 242.
22. Piratzky, W.: Ein Vorschlag zur Malzuntersuchung. In: Brauwelt 99 (1959), No. 37, pp702 – 704.
23. Qian, J. Y.; Kuhn, M.: Evaluation on Gelatinization of Buckwheat Starch: a Comparative Study of Brabender Viscoamylography, Rapid Visco-Analysis, and Differential Scanning Calorimetry. In: European Food Research and Technology 209 (1999), No. 3 – 4, pp277 – 280.
24. Scriban, R.: Neue Beobachtungen über die Hartongzahl und ihre Anwendung beim Brauen und Mälzen. In: Brauwissenschaft 16 (1963), No. 1 – 2, pp4– 11.
25. Slack, P. T.; Wainwright, T.: Amylolysis of Large Starch Granules from Barleys in Relation to their Gelatinisation Temperatures. In: Journal of the Institute of Brewing 86 (1980), No. 2, pp74 – 77.
26. Tegge, G.: Stärke und Stärkederivate. 3rd completely revised edtition Hamburg: B. Behr's Verlag GmbH & Co. KG, 2004.