

Re-Assessment of the Half-Grain Modification Method for Assessing Malt Modification

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ABSTRACT

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The half-grain mashing (modification) method proposed by Palmer (J. Inst. Brew., 1975, 81: 408) was reassessed. The intention was to quantify the differences in malt modification in terms of β -glucan breakdown and clarify the relationship between β -glucan breakdown and overall modification of the endosperm during malting. This was carried out at 45°C as well as at 65°C, the percentage of weight loss was recorded and the endosperm residue was analysed for β -glucan content. In general, weight loss was related to modification. Samples, which were modified at higher levels, lost significantly more material during the half-grain mashing procedure than those which were under-modified. At a malting process time of 96 h all the varieties had similar weight loss. After mashing the half grains, the β -glucan contents of the grain residues showed an apparent increase because of loss of non- β -glucan materials. However, over the malting period β -glucan decreased. Chariot malted faster than the other varieties studied. The β -glucan levels of this variety were reduced by 78% between 48 and 72 h of germination. Significant levels of β -glucan were degraded and large quantities of starch and protein were released. During the same period of germination, the corresponding samples of Decanter did not show a significant reduction in β -glucan levels. In contrast, Brazilian variety MN698 lost endosperm material and β -glucan rapidly by 48 h. These early results suggest that during malting, extract solubilization may or may not accompany β -glucan breakdown. Therefore, β -glucan levels in malt cannot be used as an overall index of modification of the endosperm.

Key words: Barley, β -glucan, endosperm modification, homogeneity, malt.

INTRODUCTION

In general, endosperm modification describes the conversion of the hard endosperm of barley into friable malt by the action of a mixture of hydrolytic enzymes which disaggregate and solubilize the multicellular tissue of the endosperm during malting^{13,23,26,28}. The *degree of modification* is the extent to which the endosperm is converted to malt, and can be described as poorly modified, under modified, well modified or over modified^{22,23}.

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In malting, homogeneity means that each grain within a batch of malt is modified to a similar degree. Uneven (inhomogenous) modification of the endosperm cell wall, protein and starch is not detected using Recommended Analytical Methods²⁰ of the Industry, but can cause serious processing problems for the brewer, such as, retarded wort separation, slow beer filtration and hazes²⁸.

Several factors can influence the uniformity of modification during malting of barley. These include^{4,12,25,28}: (a) conditions of steeping, which influence moisture and temperature; (b) amount of water uptake and its distribution in the grain during steeping and germination, which is related to endosperm structure and composition, as well as to the size and shape of the kernels; (c) uneven germination, which is linked to embryo viability; (d) production of gibberellic acid by the embryo; (e) effective transport of gibberellic acid through the aleurone; (f) response of the aleurone to gibberellic acid, which initiates the production of endosperm degrading enzymes; (g) distribution of enzymes through the endosperm, which is controlled by the structure of the endosperm (mealiness and steeliness); (h) the physico-chemical properties of cell wall β -glucans and storage proteins of the endosperm.

Considering the lopsided progression of modification in the endosperm during malting^{6,7}, a single grain of malt can contain a mixture of over-modified, modified and under-modified areas²⁰. Additionally, a batch of well-modified malt, in terms of total extract, may contain grains, which are under-modified. On the other hand, an under-modified sample of malt may contain grains, which are over-modified²⁶.

The development of analytical methods, which link malt specification to brewhouse performance have been the objective of brewing scientists and brewers for nearly a hundred years^{24,28}. The analytical procedures for assessing malt modification and malt homogeneity have been extensively reviewed^{16–19}. These studies suggest that in the malting and brewing industries, outdated analytical procedures continue to be applied and, because of their lack of precision, need to be revised.

Glennie Holmes studied the use of the Rapid Viscoanalyser to verify malt modification and malt quality potential^{9–11}. It was possible to monitor the progress of modification of malts using several viscogram measurements. However, the results were significant only within cultivars. None of the measurements were sufficiently accurate to predict malting potential.

A collaborative study showed that the friabilimeter has an acceptable level of precision and can determine malt homogeneity¹⁴. However, the method has limitations. Dur-

ing the friability test, milling can release under-modified endosperm flour that will pass into the friable flour fraction and be wrongly assessed as modified material^{8,29}. Furthermore, over-modified case-hardened malts can cause an under-estimation of friability scores³⁰. Additionally, the non-friable residue of different malts may contain different levels of β -glucan. High protein levels appear to cause reduced breakdown of β -glucan⁵.

The assessment of modification using sanding and staining with Calcofluor^{1,2}, which is recommended by EBC³, represented a significant development in the analysis of endosperm modification. However, Calcofluor is not specific for under-modified grains, and the method does not take into consideration the asymmetric pattern of modification of the endosperm of barley during malting. Furthermore, protein modification is not assessed with this method²⁸.

Palmer²¹ developed the half-grain mashing test to examine the inhomogeneity of endosperm modification. In this method malt grains were cut in half and then shaken in hot water (65°C) for 1 h. The modified area of the endosperm was released from the grain, leaving the under-modified areas intact. It is a qualitative test, but highlighted the range of modification that can occur in the malt grains of a sample of malt. More recently, using hand sectioning and visual inspection^{20,27} of commercial malts, the problems with wort separation and beer filtration encountered in brewhouses were shown to be related to the percentage of under-modified grains in the sample. These samples met specifications and therefore were not expected to give brewhouse problems.

Palmer²⁶ suggested that the rate at which barley samples are transformed into malt is more related to physical and chemical properties of the native cell wall of the endosperm than the levels of β -glucan which are extracted from the endosperm. It has been demonstrated that β -glucan composition and water solubility are important influences on water uptake during malting. The water insoluble fraction can act as a barrier to water, while the soluble fraction can act as a sponge, facilitating water uptake¹⁵. This may have a great influence on the rate of modification of the endosperm, because water is important for the diffusion and action of hydrolytic enzymes in the endosperm.

The primary aim of this study was to reassess the half-grain modification test, developed in 1975²¹. The intention was to quantify the differences in malt modification in terms of β -glucan breakdown and clarify the relation-

ship between β -glucan breakdown and overall modification of the endosperm during malting.

MATERIALS AND METHODS

Barley quality and malting

For this study the barley samples used were from the United Kingdom and Brazil. British varieties were Decanter and Chariot, harvested in 2000 and 2001, respectively, supplied by the Home Grown Cereals Authority (HGCA, London). Brazilian varieties were MN698 and BR2, harvested in 2000 and kindly supplied by AmBev – Companhia de Bebidas das Américas.

Extraneous matter and small grains (< 2.2 mm) were removed. The germinative energy and total nitrogen content of the barley varieties were determined. Barley samples (300 g) were steeped at 16°C. A first steep of 8 h was followed by 16 h air rest and a 24 h final steep. A Seeger micro-malting unit was used⁶. Germination was for four days, at 16°C. Germinative percentages were checked daily. Samples were collected after 48, 72 and 96 h of germination, and kilned at 65°C, for 16 h.

Half grain mashing

This method directly determines the status of modification of individual malt grains. The kernels were cut in half sections longitudinally and extracted in water at 65°C²¹. In this study, the method was modified and the cut grains were washed at 45°C and 65°C, respectively. Both experiments were carried out in triplicate for each sample of malt.

45°C experiment. 100 grains of each malt sample (in triplicate), were cut longitudinally through the acrospire into halves, using a one-edge razor blade. The 100 half grains were milled using a coffee mill (Moulinex, type 505, Ireland), weighed and analysed for content of moisture and β -glucan. The remaining 100 half grains were put into a 250 ml bottle (Schott Duran, Germany) and 50 ml of distilled water pre-warmed at 45°C was added. The bottles were placed into a shaking water bath (Gallenkamp, UK) at 45°C and washed with continuous shaking for 1 h²¹. After this period, the half grains were drained and transferred to a petri dish and dried overnight in oven at 55°C. After drying, the grains were milled in a coffee mill, weighed and analysed for moisture and β -glucan content³. Only malt samples from the British varieties were used in this experiment.

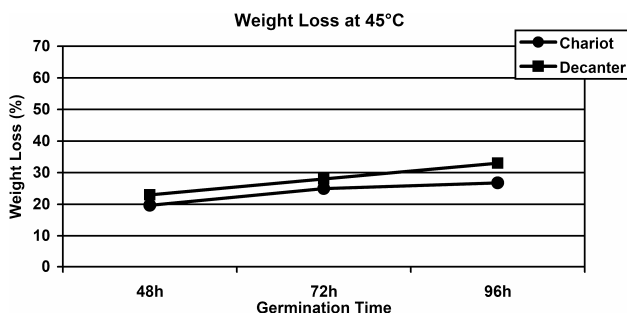


Fig. 1. Weight loss (%) after mashing 100 half grains at 45°C.

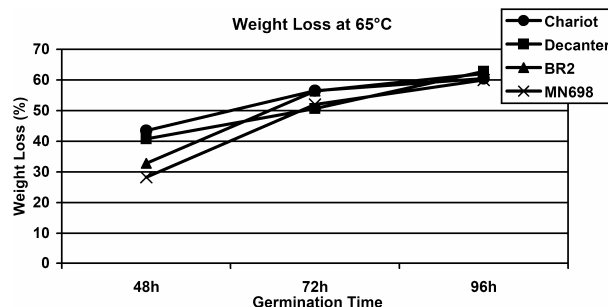


Fig. 2. Weight loss (%) after mashing 100 half grains at 65°C.

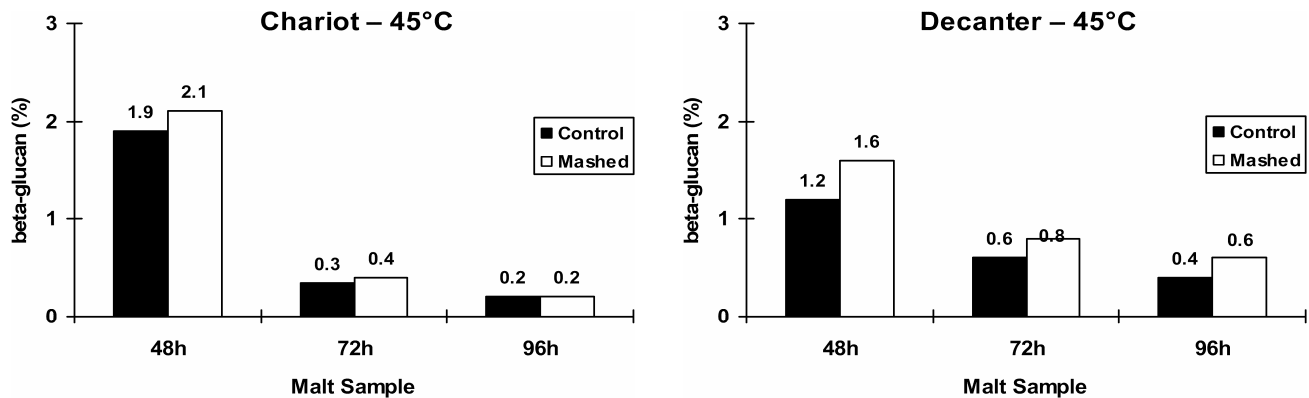


Fig. 3. β -Glucan (%) content of control and mashed half grains (100) at 45°C, varieties Chariot and Decanter.

65°C experiment. The procedure followed was the same as above, with the temperature at 65°C, instead of 45°C²¹. British and Brazilian malt samples were tested.

Statistical analyses

Statistical analyses of data were performed using Minitab® (Minitab Inc., release 13.1) and S-PLUS® (Insightful Corp., release 6.2 for Windows). The methods used were General Linear Model and ANOVA, comparisons of means, descriptive statistics, distribution and correlation. Where not stated, results presented are an average of triplicate analysis.

RESULTS AND DISCUSSION

Assessment of endosperm modification by half grain mashing

In 1975²¹, a new modification method was proposed. It provided means of measuring endosperm modification directly, without disruptive treatment of the cut grain. In this method malt grains were cut in half and then shaken in hot water (65°C) for 1 h. The modified area of the endosperm was released from the grain, leaving the under-modified areas intact. In this experiment, instead of assessing modification visually, residues of half-grains were dried and ground, and then analysed for β -glucan content. The other halves of the grains of each sample, which were not washed, were also ground, analysed for β -glucan content and used as a control. The percentage weight loss for each sample was recorded. The intention was to try to quantify in terms of differences in weight and β -glucan, the differences in modification that had occurred in the samples of malt.

The percentages of weight loss after mashing at 45°C and 65°C, are presented in Figs. 1 and 2 respectively. The results presented are the mean values for triplicate experiments. There was a significant effect of variety and length of germination on the percentage of weight loss, for the 45°C experiment. Variety and length of germination, as well as the interaction of these two factors had significant effects on the percentage of weight loss for the 65°C experiment.

In the 45°C experiment (Fig. 1), the differences in weight loss observed were small, but it was possible to observe an increase in the loss of endosperm material as germination progressed. The highest percentages of weight

loss were for malt samples at 96 h of germination. These had the highest degrees of modification^{6,7}.

In the 65°C experiment (Fig. 2), all the varieties lost more material as germination time increased. The Brazilian varieties, MN698 and BR2, were significantly different from the others in terms of weight loss, having lost less material.

In the 45°C experiment (Fig. 1), Decanter had a higher overall percentage of weight loss than Chariot. However, for the 65°C experiment (Fig. 2), even though the 96 h samples from Decanter and Chariot had the same percentages of weight loss, Chariot had higher weight loss for the 48 and 72 h samples. This suggested a higher percentage of modified material was being extracted faster from Chariot malts during mashing.

All the varieties had a higher weight loss in the 65°C experiment than in the 45°C experiment, suggesting that hot water mashing is an important aspect of solubilization of endosperm material.

When washing the half grains and extracting the modified material, the overall concentration of under-modified material, such as β -glucans, showed an apparent increase in quantity. Figs. 3 and 4 show β -glucan percentage of the control (unmashed) and mashed samples, in the 45°C and 65°C experiments, respectively.

The histograms show what could be important information regarding endosperm modification and the rate that each variety modified during germination. Regarding the samples mashed at 65°C, for Chariot, β -glucan levels fell 78% between 48 and 72 h, showing significant β -glucan breakdown and significant release of starch and protein (Fig. 4). During this period of germination, the β -glucan levels for the corresponding samples of Decanter did not fall significantly. However, after 96 h the β -glucan levels of Decanter fell by 53%.

These results confirm that Decanter malt is slower, in terms of endosperm modification than Chariot. They also confirm the results obtained for physical modification presented elsewhere^{6,7}, and that the rate of modification of the endosperm is not entirely related to the initial content of β -glucan in a sample of malt, because Chariot had higher β -glucan levels than Decanter initially (Fig. 4).

The variety BR2 showed a decline of 60% in β -glucan between 48 and 72 h, and the levels continued to decrease until 96 h. MN698 was slower and β -glucan declined 40% between 48 and 96 h of germination.

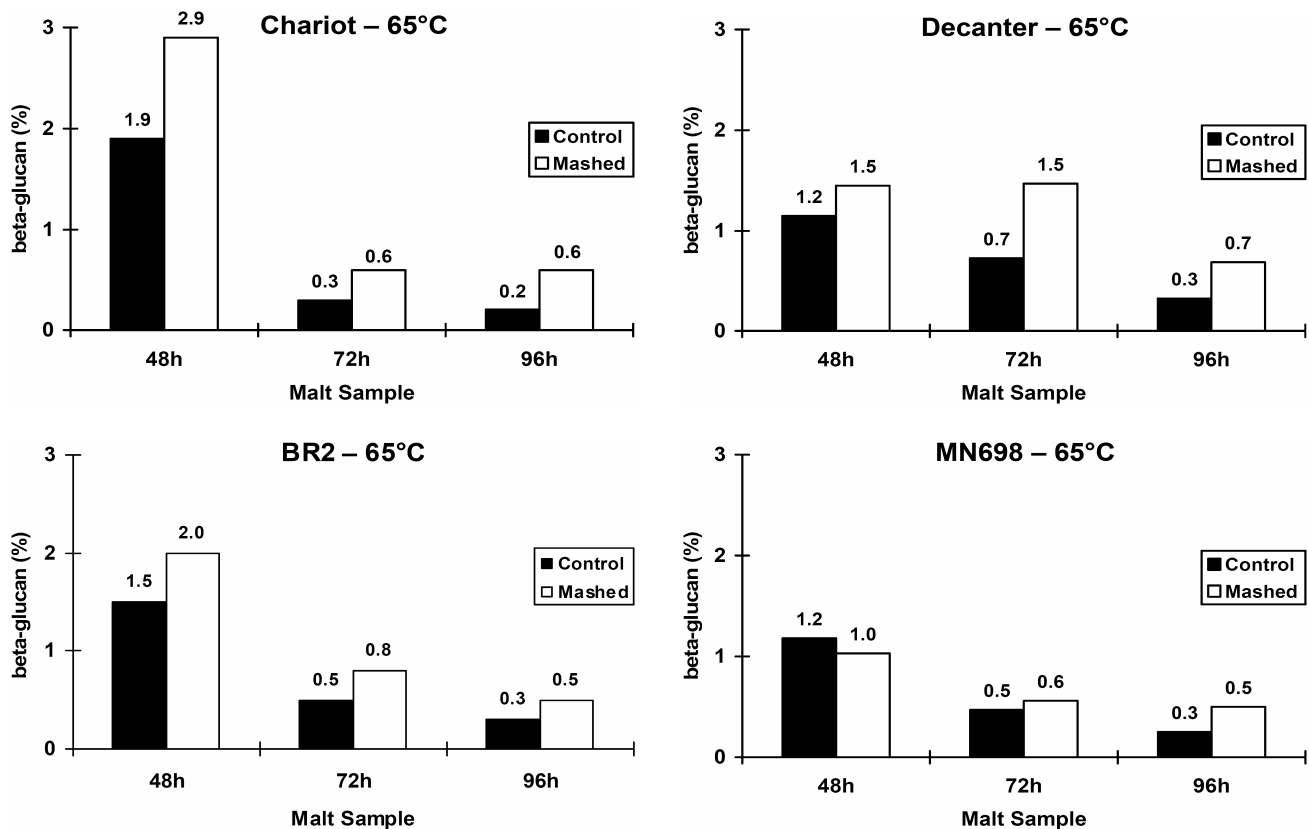


Fig. 4. β -Glucan (%) content of control and mashed half grains (100) at 65°C, varieties Chariot, Decanter, BR2 and MN698.

Regarding the 45°C experiment, Chariot showed a faster rate of endosperm modification than Decanter, with an 81% decrease in β -glucan levels between 48 and 72 h. In addition, Decanter had a decline of 50% in β -glucan levels between 48 and 72 h, which did not occur in the 65°C experiment, suggesting that a 45°C mash may give an important indication of β -glucan modification during malting.

In general, these results suggest that loss of endosperm materials (modification) occurred most rapidly in Chariot, causing initially high percentages of β -glucan, followed by a rapid decline in β -glucan from 48 to 96 h of germination (malting). MN698 lost endosperm material and β -glucan rapidly by 48 h.

It would appear that during malting, extract solubilization and release may or may not accompany β -glucan breakdown. Therefore, β -glucan levels in malt cannot be used as an overall index of modification (solubilization) of the endosperm.

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