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## INFLUENCE OF MALTING PROCEDURE ON THE QUALITY OF HULLESS BARLEY MALT

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### ABSTRACT

This paper investigated the influence of malting procedure on quality indicators of hulless (naked) barley malt according to the recommended values for standard pale malt. The aim was to determine the optimal malting procedure in order to achieve the best results for investigated indicators in relation to the recommended values. Two domestic hulless barley varieties (Matko and GZ-184) were malted and four malting procedures were applied: (A) standard procedure – control; (B) gently intensive procedure with uniform temperature increase during germination till the end of the process; (C) moderately intensive procedure with the increase of germination temperature on the second and third day, and constant germination temperature till the end of the process; (D) procedure with sudden germination temperature decrease after the first day, and constant temperature till the end of the process. The influence of four malting procedures on soluble N content in malt, total N and soluble N ratio (Kolbach index), Hartong number, friability, extract, fine/coarse difference, colour, boiled wort colour, pH, viscosity and filterability of wort, and  $\beta$ -glucans were investigated. Based on obtained results, and their comparison to results reported in scientific and technical literature, the efficacy of each micromalting procedure was evaluated, considering recommended values for hulless barley malt. The results indicate that the resistance to deeper modification of grain (expressed as lower water absorption during soaking grains, and as weaker friability) are the main problem that will need to be solved in the further selection processes of domestic hulless barley varieties for malting. The intensification of the process of germination should be combined with the extension of soaking time, which should lead to improvements of friability of malt and better value for other indicators of malt quality.

**Keywords:** Croatian hulless barley varieties, malting quality, malting procedure

### INTRODUCTION

Most barley varieties are hulled. If the hull does not adhere, the barley is considered to be hull-less or hulless. One gene (NUD) determines whether or not the hulls (lemma and

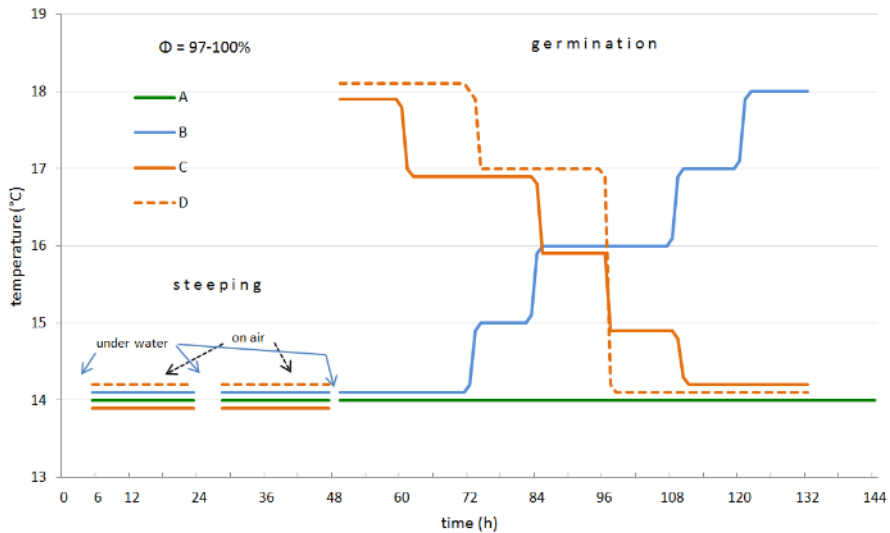
palea) adhere to the grain (Taketa *et al.*, 2008). This particular barley variety, *Hordeum vulgare* L. var. *nudum* Hook. f. has a loosely attached hull and during harvest the hull falls off by itself which makes the further processing much easier and more economy friendly reducing germ damage and flour loss during milling. This interest in development of new varieties of hullless barley started in the 1970' in Canada. Firstly, this kind of barley was used as stock feed, and then it became interesting for human nutrition and expanded as a new raw material for malt in brewing and distilled products (drink such as Scotch). Croatian agro-science also tried to keep up with the trends and during this period a variety "Osječki golozrni" was created, but it did not make it to production. Currently, there is only one Croatian variety of hullless barley, named Matko, but some new varieties are being developed at Agronomic Institute in Osijek. Hullless barley is also well known for its positive physiological effects and recognized as functional food. It has abundance of dietary fibre, and it is also rich in mineral elements, such as calcium, phosphorus, iron, copper, zinc, and selenium, materials which play a vital role in promoting human health. Nevertheless, its application in brewing industry is still a novelty and was firstly introduced with the development of new varieties with desirable malting properties. In short, the most important advantage of hullless barley usage in brewing industry is the economical aspect since hullless barley significantly increases malt extract 5–7 % (minimally > 2) respectively to hulled barley (Kerry & Barr, 1995; Edney & Langrell, 2004; Zhou *et al.*, 2012; Evans *et al.*, 2014; Rossnagel *et al.*, 2012). Approximately 90 % of this increase is caused because the hull is absent (hull makes 10 % of dry matter loss in barley grains) (Rennecke & Sommer, 1979). The lack of hull during mashing helps in eliminating the extraction of specific polysaccharides from hulls, which have been identified to cause premature yeast flocculation during fermentation (Edney & Langrell, 2004). Spent grain amount is also reduced with the use of hullless malt. Thus, multiple application of hullless barley are possible in malting and brewing processes. Improvements in beer quality may be possible due the absence of undesirable hull compounds such as tannins and other polyphenols. In the past, the use of hullless malt has been restricted because intact hulls affected the efficiency of lautering operation. However, with the advent of newer technologies for spent grain separation, such as mash filters and centrifuges, there has been increased interest in the advantages of hullless barley malt (Evans *et al.*, 2014). Alongside listed benefits of hullless barley usage in malting and brewing, there are also some disadvantages: the malting of hullless barley, however, presents a number of challenges due to differences in chemical and physical characteristics; the missing hull makes the barley susceptible to embryo damage during handling and malting; the loss of embryo, at an inopportune time, can prevent adequate endosperm modification. Poor, unacceptable modification has been a major concern (Evans *et al.*, 2014), which could be related to embryo loss and a resulting poor or incomplete germination (Box & Barr, 1999). Poorly modified or incompletely degraded grains are related to many undesirable quality characteristics of dry malt (Edney & Langrell, 2004; Evans *et al.*, 2014). The poor modifications observed in malt obtained from hullless barley could explain some of the reduced level of extract, since unmodified cell walls are known to restrict starch hydrolysis and, therefore, the solubilization of starch during mashing (Evans *et al.*, 1999). Friability values for malt from hullless barley have been much lower than the values acceptable for

hulled barley malt (Edney & Langrell, 2004). Furthermore, water uptake during steeping is much quicker in hulless barley than in hulled (covered) barley (Sing & Sosulski (1985). Bhatti (1986) also found hulless barley to be harder than hulled malting barley; standard malting conditions have to be altered in order to adequately process hard, steely barley and prolonged steeping and germination times may be required. Kilning step may also cause a problem. Without the protection of a hull, high kilning temperatures may cause hulless malt to become extra hard. The effects of modified malting conditions applied to two domestic hulless barley varieties (Matko and GZ 184) were investigated in this paper. Four malting procedures were applied: (A) standard procedure – control; (B) gently intensive procedure with uniform temperature increase during germination till the end of the process; (C) moderately intensive procedure with the increase of germination temperature on the second and third day, and constant germination temperature till the end of the process; (D) procedure with sudden germination temperature decrease after the first day, and constant temperature till the end of the process. Considering the stated information, this research was to assess the quality of available varieties of hulless barley from the brewing point of view and to assess how will these varieties respond to changes in process parameters during the malting process considering the set values of quality indicators of standard dry malt.

## **MATERIALS AND METHODS**

Hulless barley samples were obtained from field trials of the Institute of Agriculture Osijek in 2013, 10 kg of each variety (Matko and GZ-184). Grain samples were collected as untreated and conditioned grain, scaled and packed into in double-walled paper bags (1 kg). Until micromalting the material was stored for two months in a dry and cool place (20 °C) to overcome post-harvest grain dormancy. Determination of standard starting quality indicators of this barley varieties was conducted in the laboratory of the Institute of Agriculture Osijek.  $\beta$ -glucan content was determined in the Laboratory for cereal technology at the Faculty of Food Technology Osijek. Micromalting procedure was performed according to MEBAK (MEBAK, 2.5.3.1.) in order to determine the brewing quality of selected varieties and was conducted in the micromalting plant Joe White Malting Systems (Pty. Limited East Melbourne, Victoria, Australia; Automatic Micro Malt Unit, 10 kg capacity). Degermination of dry malt was performed manually. This malting procedure was tagged as (A), control sample. Four kg of each barley variety was micromalted and after the micromalting malt samples were weighed on 500 g samples and stored in paper bags for one month in order to stabilize. Same samples served for three more modified micromalting procedures (B, C and D) in order to asses dry malt quality when applying different process conditions. These micromalting procedures were conducted in the same micromalting plant, and the germination process temperatures are displayed in Fig. 1. Germination was conducted in Climatic test chamber (Climacell 222, Medcenter Einrichtungen GmbH). Modified Micromalting were conducted according to MEBAK, but dependent on case to case, the last steeping (third day) can also be considered as the first day of germination. This applies in cases the grain cannot endure three steeping days (in this case the third steeping meant that the grain moisture was adjusted by

sprinkling in the germination chamber). The humidity in the beginning of germination was set to 45 % (44 % + 1% surface water). It is useful to mention that the modified malting procedures is actually a simulation of process parameters adjustment in the industrial scale. This implies adjustment to starting raw material quality in order to obtain the best malt possible. Procedures are modified in the germination phase. As this is the first research of this kind for Croatian hulless barley varieties, the modification procedures in this paper were set to the extreme values (B) and (C). It was assumed that the hulless barley is more like wheat, so the procedure for wheat micromalting was applied (Sacher, 1998; Narziß, 1999).



**Figure 1.** Micromalting scheme of hulless barley samples.

This is actually the standard procedure for barley (MEBAK, 2.5.3.1.) but with slight modification of steeping time and air humidity during germination 95 % ( $\pm 1$  %) because hulless barley soaks up water much quicker than barley. Humidity decrease helps to avoid possible draining of the piles (the possibility of uncontrolled increase of moisture of germinating grain is prevented). Uncontrolled moisture increase of grains affects almost all quality indicators. Problems related with malting of hulless barley are that it is much harder than wheat and it has much lower friability than hulled barley. This is why moisture of piles was set to be 95 %, while germination time (longer in this case in order to obtain a better grain degradation) was not changed. The end of germination was determined visually after the third day (according to the length of acrospires). This way of germination control is essential in order to stop the appearance of hussars ( $>3$  %) and

to enable the grains to germinate uniformly. The leading idea for the application of procedures shown in Fig. 1 was to, by the usage of restrictive procedure B (increasing germination temperatures) and the intense procedure C (decreasing germination temperatures), assess the behaviour of each variety during malting procedure and to notice its resistance in maintaining the key variety trait (i.e. enhanced tendency for proteolysis and cytolysis) under different malting conditions. If a variety is more inclined to higher proteolysis during standard micromalting procedure A, than this trait will be even more expressed during micromalting procedure C. Contrary, the same variety will give satisfactory values for quality indicators if procedure B is applied during micromalting. The same can be applied inversely on a certain indicator which is connected with a certain property, for example the suitability of variety for cytolytic degradation (viscosity, soluble  $\beta$ -glucans concentration or extract difference). These results should serve as quality indicator of investigated varieties, although malting in industrial scale implies that process parameters are set to provide the best results for quality indicators of malt. As an additional contribution in order to establish the most appropriate malting scheme, a moderately intense procedure D was conducted Fig. 1. This procedure consisted of process parameters adjusted to obtain acceptable values for both quality indicator groups (proteolytic and cytolytic) Fig. 1, which are usually mutually contradictory. Dry malt samples were analysed according to EBC-Analytica in the IREX Group laboratory (STAMAG Stadlauer Malzfabrik GesmbH, A-Wien), except  $\beta$ -glucan content in barley samples determined using Mixed-Linkage  $\beta$ -Glucan kit (enzyme method) (AACC, 2006). Four samples of 1 kg of each barley variety was malted and mean values (mean  $\pm$  SD) are shown in Tab. 2. Determination of the influence of a certain malting procedure on the chosen quality indicators was compared by Fisher's Least Significance Test ( $p \leq 0.05$ ).

## RESULTS AND DISCUSSION

As previously stated, hullless barley related problems are connected with cytolytic degradation and are directly related with  $\beta$ -glucan content. If we compare  $\beta$ -glucan content in both barley varieties tested in this research (Tab. 1) and their malts (Tab. 2), it is visible that  $\beta$ -glucan content is much higher in malts, than in starting barley.  $\beta$ -glucan content is significantly influenced by germination procedures A and D for GZ-184 variety, while B and C procedures did not cause any significant changes in  $\beta$ -glucan content. Matko's  $\beta$ -glucan content does not appear to be influenced by malting procedure in any of the applied procedures (Tab. 2).

On the other hand, if we compare  $\beta$ -glucan and friability values for each variety (Tab. 2), the influence of germination procedure is more visible. Namely, viscosity values are connected with friability values, meaning that higher friability values make wort viscosity lower. This indicates the connection of deeper grain degradation with different components which cause the increase of wort viscosity values ( $\beta$ -glucans, pentosanes, residual starch) which is in accordance with previous research (Sing & Sosulski, 1985; Evans *et al.*, 1999; Evans *et al.*, 2014;).

**Table 1.** Quality characteristics of hulless barley cultivars (GZ- 183 and Matko, harvest 2013)

| Physical analysis:      |                                  |                    | GZ - 184 | Matko |
|-------------------------|----------------------------------|--------------------|----------|-------|
| 1.                      | Gradin                           | - above 2.8 mm (%) | 74.2     | 77.4  |
|                         |                                  | - above 2.5 mm (%) | 22.3     | 26.2  |
|                         |                                  | - I class          | 94.3     | 91.0  |
| 2.                      | Thousand corn weight (g dry wt.) |                    |          |       |
| 3.                      | Filtth (%)                       |                    | 1.72     | 2.06  |
| Physiological analysis: |                                  |                    |          |       |
| 5.                      | Germinative energy (3 days)      |                    | 96       | 98    |
| 6.                      | Germinative energy (5 days)      |                    | 99       | 99    |
| Chemical analysis:      |                                  |                    |          |       |
| 7.                      | Moisture content of grain (%)    |                    | 11.64    | 11.38 |
| 8.                      | Total proteins (% dm) f=5.7      |                    | 13.80    | 13.20 |
| 9.                      | β-glucan (g/100 g dm)            |                    | 4.05     | 4.62  |
| 10.                     | Starch content (%)               |                    | 61.80    | 62.00 |

Lowest, more acceptable values for viscosity are obtained using procedures A and D for hulless barley GZ-184 (Tab. 2). These values stand out from values obtained from other applied malting procedures since they all caused higher viscosity values. Tab. 2 shows the narrow connection of  $\beta$ -glucan content and viscosity in a way that the lower  $\beta$ -glucan content, the lower the viscosity. This is also in accordance with previous research (Zhou *et al.*, 2012; Evans *et al.*, 2014).

Extract difference of fine and coarse grind is an indirect measure of malt modification (Briggs, 1998). A significant difference between malt extracts indicates the presence of large parts of non-degraded endosperm which have lower enzyme activity (giving lower wort quality). Extract difference also follows friability in a way that the increase of friability causes extract difference decrease and, consequently, congress wort viscosity decrease. It is interesting to notice that in regards to wheat, hulless barley has a much lower friability values (Bhatty, 1986) even though its water absorption is much better. This clearly indicates the existence of hardly degradable endosperm zones, even with such good grain moisture which should enable good enzyme activity. Hartong number (VZ 45 °C) is an indicator of enzyme activity at 45 °C (mainly cytolytic and proteolytic enzymes).

**Table 2** Malt quality indicator analysis

|                       |                                 | Micromalting procedure |                   |                   |                   |                    |                    |                   |                   |
|-----------------------|---------------------------------|------------------------|-------------------|-------------------|-------------------|--------------------|--------------------|-------------------|-------------------|
|                       |                                 | A                      |                   | B                 |                   | C                  |                    | D                 |                   |
| Indicator / unit<br>→ | Varieties                       | Matko                  | GZ-184            | Matko             | GZ-184            | Matko              | GZ-184             | Matko             | GZ-184            |
| 1.                    | Moisture content (%)            | 8.4                    | 8.4               | 9                 | 8.6               | 8.9                | 9.2                | 8.9               | 8.9               |
| 2.                    | Fine grinde extract (% dm)      | 69.4                   | 82                | 60.6              | 68.8              | 59.7               | 70.3               | 70.6              | 80.5              |
| 3.                    | Coarse grind extract (% dm)     | 58.4                   | 78.5              | 47.6              | 62.3              | 45.6               | 64.2               | 65                | 77.9              |
| 4.                    | Extract difference (%)          | 9 <sup>c*</sup>        | 3.5 <sup>f</sup>  | 13 <sup>b</sup>   | 6.5 <sup>d</sup>  | 14.1 <sup>a</sup>  | 6.1 <sup>de</sup>  | 5.6 <sup>e</sup>  | 2.6 <sup>f</sup>  |
| 5.                    | Saccharification rate (min)     | 15                     | 15                | 60                | 20                | 60                 | 20                 | 20                | 15                |
| 6.                    | Clarity of wort (EBC unit)      | 4                      | 1                 | 4                 | 4                 | 4                  | 4                  | 5                 | 1                 |
| 7.                    | Attenuation limit (%)           | 78.5                   | 80.0              | 66.5              | 72.8              | 71.1               | 77.4               | 79.3              | 79.8              |
| 8.                    | Filtration time (min)           | R                      | R                 | L                 | R                 | L                  | R                  | R                 | R                 |
| 9.                    | Odour of mash                   | N                      | N                 | N                 | N                 | N                  | N                  | N                 | N                 |
| 10.                   | Protein (% dm) f=6.25           | 13.1 <sup>b</sup>      | 12.3 <sup>d</sup> | 13.4 <sup>b</sup> | 13 <sup>b</sup>   | 13.4 <sup>ab</sup> | 13.4 <sup>ab</sup> | 13.4 <sup>a</sup> | 12.6 <sup>c</sup> |
| 11.                   | Nitrogen (% dm)                 | 2.1                    | 1.97              | 2.14              | 2.08              | 2.14               | 2.14               | 2.14              | 2.02              |
| 12.                   | Soluble protein (% dm)          | 3.4 <sup>c</sup>       | 4.9 <sup>a</sup>  | 2.6 <sup>d</sup>  | 3.6 <sup>c</sup>  | 2.4 <sup>d</sup>   | 3.9 <sup>b</sup>   | 4.1 <sup>b</sup>  | 5.1 <sup>a</sup>  |
| 13.                   | Soluble nitrogen (g/100 g dm)   | 0.55                   | 0.78              | 0.42              | 0.58              | 0.38               | 0.63               | 0.66              | 0.82              |
| 14.                   | FAN (mg/L)                      | 117                    | 174               | 86                | 126               | 83                 | 133                | 150               | 204               |
| 15.                   | Hartong VZ 45 (%)               | 33.9 <sup>bc</sup>     | 48.1 <sup>a</sup> | 24.7 <sup>d</sup> | 34.3 <sup>c</sup> | 25 <sup>d</sup>    | 33 <sup>c</sup>    | 39.5 <sup>b</sup> | 48.4 <sup>a</sup> |
| 16.                   | Kolbach index (%)               | 26 <sup>d</sup>        | 40 <sup>b</sup>   | 20 <sup>e</sup>   | 28 <sup>c</sup>   | 18 <sup>f</sup>    | 29 <sup>c</sup>    | 31 <sup>c</sup>   | 41 <sup>a</sup>   |
| 17.                   | Colour of wort (EBC unit)       | 3                      | 2.6               | 2.5               | 2.7               | 2.4                | 2.6                | 3.1               | 2.9               |
| 18.                   | Colour after cooking (EBC unit) | 3.5                    | 5                 | 2.8               | 3                 | 2.8                | 3.3                | 4                 | 6.2               |
| 19.                   | Viscosity (mPa×s. 8.6%e)        | 2.17 <sup>a</sup>      | 1.65 <sup>d</sup> | 2.17 <sup>a</sup> | 2.15 <sup>a</sup> | 2.17 <sup>a</sup>  | 1.9 <sup>b</sup>   | 1.78 <sup>c</sup> | 1.62 <sup>d</sup> |
| 20.                   | Friability (%)                  | 29 <sup>b</sup>        | 35 <sup>a</sup>   | 19 <sup>de</sup>  | 24 <sup>c</sup>   | 18 <sup>e</sup>    | 21 <sup>d</sup>    | 31 <sup>b</sup>   | 35 <sup>a</sup>   |
| 21.                   | Glassy grains (%)               | *                      | *                 | *                 | *                 | *                  | *                  | *                 | *                 |
| 22.                   | Partly glassy grains (%)        | *                      | *                 | *                 | *                 | *                  | *                  | *                 | *                 |
| 23.                   | β-glucan (mg/L)                 | 500 <sup>a</sup>       | 320 <sup>b</sup>  | 500 <sup>a</sup>  | 500 <sup>a</sup>  | 500 <sup>a</sup>   | 500 <sup>a</sup>   | 500 <sup>a</sup>  | 355 <sup>b</sup>  |

\* due to extreme low friability nearly all grains could be rated as glassy or partly glassy

\*\*Mean values followed by the same letter in the same row are not significantly different (LSD) test ( $p < 0.05$ )

\*\*\*R – regular; L– lower; N – normal

This research showed optimal Hartong number when using B and C procedures. With the decrease of β-glucan content (better degradation of β-glucan), VZ 45 °C values showed an increase in A and D procedures (Tab. 2). Malt extract is usually a basic economic indicator



of malting procedure and grain quality, representing all water-soluble components (fermentable and non-fermentable) transferring to wort during mashing. Tab. 2 shows that less extract was obtained with the increase of  $\beta$ -glucan content. Malting procedures, A and D of GZ-184 variety (2 and 8) gave higher extract values and  $\beta$ -glucan content was lower. Saccharification rate was optimal for all malting procedures, except procedures B and C for Matko variety where saccharification rate lasts longer (Tab. 2). When looking at proteolytic degradation indicators, a relatively high total protein content in barley and malt (Tab. 1 and Tab. 2) is followed by very low soluble proteins content. Low soluble proteins content can be caused by weak grain degradation (low friability) which in consequence lowers the values of many malt quality indicators. Soluble proteins and FAN content of obtained malts show that both indicators are suitable for both varieties, except in malting procedures A and D for GZ-184 (Tab. 2).

## CONCLUSIONS

The resistance to a deeper grain modification (expressed as weaker water absorption in steeping phase and lower friability values) is obviously the core problem and it will need to be dealt with when selecting new hulless barley varieties for malting industry. The intensification of malting procedures made no significant alterations of chosen quality indicators. High  $\beta$ -glucan content is a reason for weaker water absorption in some zones of the endosperm and a lower enzyme activity which makes the grain poorly modified during malting. This directly distorts all other indicators related with friability (extract, extract difference, Kolbach index, Hartong number and wort viscosity). The intensification of germination procedure should be combined with the extent of steeping time which should affect the overall malt quality indicators, including the friability.

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