150

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Selective steering of roasting process to reduce prooxidative effects of roasted malt

Thomas Kunz[1], Clemens Kanzler[1], Hans Fröhlich[1], Martina Gastl[2], Frank-Jürgen Methner[1]

[1]Technische Universität Berlin, Institute of Food Technology & Food Chemistry, Germany; [2]Technische Universität Weihenstephan, Department of Biotechnology, Germany

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INTRODUCTION

The influence of roasted malt on the oxidative beer stability has been reported controversial by different authors [1,2,3,5,6]. The high temperatures during roasting of malt contribute to the formation of Maillard reaction products, which are jointly responsible for the characteristic color and flavor of the final beer. Because of their variety, these products can participate in numerous reactions during mashing, wort boiling and beer storage. They can act beneficially as well as detrimentally on the oxidative beer stability as already reported [1–5]. Particularly, reductones formed in the Maillard reaction are generally known for their high reactivity.

Our recent studies have shown that the usage of roasted malt in general leads to a decrease of oxidative wort and beer stability. In consequence, a more rapid SO_2-consumption rate and a stronger formation of specific aging components during brewing and beer storage are observed. The acceleration of prooxidative processes mainly arises from the strong reduction properties of specific Maillard reaction intermediates with reductone structure like the α-dicarbonyls (1-deoxyglucosone[11], glucosone and maltosone). These reaction products rapidly reduce metal ions like Fe^{+3} and thereby intensify the Fenton reaction system. In a chain of reactions an acceleration of oxygen activation by electron transfer and a stronger radical generation of very reactive radicals (e.g. OH•)is observable. Furthermore, a significant release of metal ions caused by roasting additionally contributes to the described prooxidative processes.

Fenton-Reaction: $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^-$ $(k_1 = 63\ M^{-1}sec^{-1})$

$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + O_2^{-\bullet} + 2\,H^+$ $(k_2 = 0.01\ M^{-1}sec^{-1})$

Net: $2\,H_2O_2 \xrightarrow{Fe} OH^{\bullet} + OH^- + O_2^{-\bullet} + 2\,H^+$

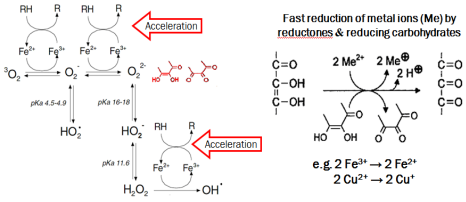

Fig. 1: Acceleration of oxygen activation and radical generation (Fenton-Reaction) by specific Maillard intermediates with reductone structure

Contact: **Thomas Kunz**
thomas.kunz@tu-berlin.de,
+49 (30) 314-27 400

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SAMPLE PREPARATION / ANALYTICS

Sample preparation:

- Malting: MEBAK[9] method 1.5.3
- Roasting scheme according to Fig. 2
- Roasted kernel extraction: 70g roasted kernels + 230 ml hot bidest. water; extraction at 97°C for 135 min; separating by Büchner funnel + rinsing kernels with 75ml hot bidest. replenish to 110 ml

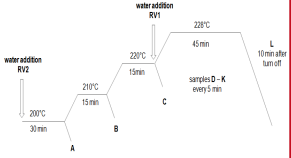


Fig. 2: Roasting scheme

Analyses:

- **Color:** MEBAK[8] method 2.12.2
- **Extract:** MEBAK[8] method 2.9.6.3
- **Iron concentration:** ICP-OES system with CID 86 detector, RF power: 1150 [W]; argon gas flow rates: 0.5 [L/min], sample: 4.0 [mL/min]; emission lines: 239.5,259.9 [nm]
- **Reductones:** 5 ml roasted kernel extracts are derivatized with 1 mL 0,05 M ortho-phenylendiamin solution at room temperature for 24h and stored at -18°C. Subsequently clarified with a syringe filter and analysed via HPLC-DAD.
- **ESR measurements: Endogenous Antioxidative Potential (EAP); T_x-determination[7]:** according to Kunz et. al: MEBAK[8] method 2.15.3 as shown in fig. 3

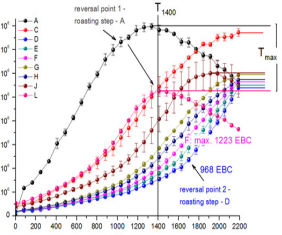


Fig. 3: EAP, T_{max}/T_{1400} -determination of roasted kernel extracts

RESULTS

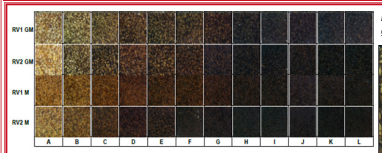


Fig. 4: roasting stages of green malt and malt

Fig. 5: kernels of roasted green malt after 60 min.

Fig. 6: RV2 green malt after 60 minutes

In general, it can be observed that the color of kernels continuously gets darker with roasting time and that malt with water addition before roasting (RV 2) gets dark faster than with sprinkling after 60 min (RV 1). Furthermore, green malt (GM) needs a higher thermal load to yield the same color as roasting malt (M) (fig. 4), but the color of the kernels is not directly transferred into the corresponding extract (fig. 7). As shown in fig. 6 the rootlets of green malt get black after 60 min of roasting, while the kernels stay pale. However, fig. 5 shows that even if the husk of the kernel appears still pale, the encosperm can already be coloured very dark.

RESULTS

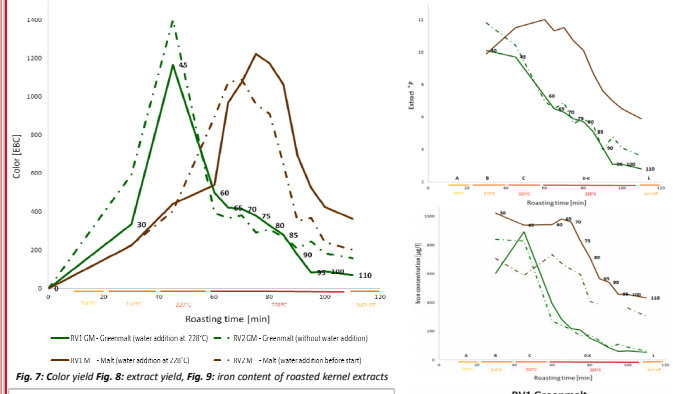
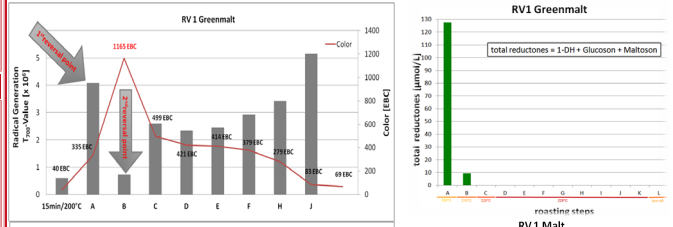


Fig. 7: Color yield *Fig. 8: extract yield,* *Fig. 9: iron content of roasted kernel extracts*



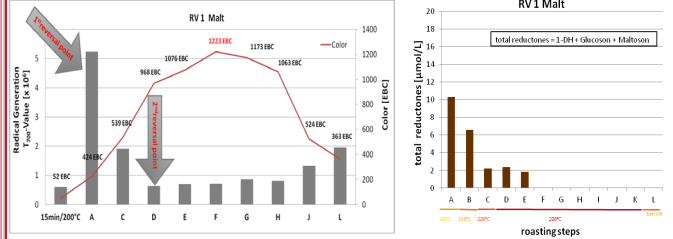


Fig. 10: T_{700} – values and color yield at different roasting stages of green malt and malt

Fig. 11: Total Reductones

CONCLUSION

Roasted green malt and malt reach about the same color level (1200 EBC, fig. 7). The color maximum of green malt appears after 45 min. (200/210°C). Roasted malt shows a later and longer period of maximum color yield between 60-80 min. This is due to the fact that the reaction rate for color formation is much higher with increased water content of the raw material [10]. In correlation to the green malt extract yield (fig. 8), the color yield is suddenly reduced direct after maximum within 15-20 min, whereas the roasted malt shows a later color and extract decrease after 85-90 min (H). It is visible that the significant increased prooxidative iron entry caused by roasting process and pyrolysis (fig. 9) starts to decrease before highest color yield.

The reductone determination (fig. 11: α-dicarbonyl = 1-Deoxyglucosone + Glucoson + Maltoson) demonstrates the connection between generation and decomposition of prooxidative acting Maillard intermediate products in dependency to the raw material and roasting conditions. At beginning of roasting the reductone conten correlates with the detected influences on oxidative stability as indicated by the analysed prooxidative radical generation (T_{700}-values) using ESR spectroscopy (fig. 10). The highest reductone content can be detected after 30 min at 200°C in green malt followed by roasted malt on a significant lower level (fig. 11). Shortly after the maximum is a rapidly decrease in the reductones and radical generation (T_{700}-value) visible. Thereby shows the green malt a significant stronger decrease in comparison to malt. Consequently a very low reductone content and T_{700}-value can be detected (B). Whereby the following intermediates of Maillard reaction show no more pro-oxidative properties up to the over roasting. The same effect on the reductones and T-value can be observed with roasted malt after 60 min (D). The lowest prooxidative properties can be detected in the time frame of the maximum color yield and indicate a second reversal point. This indicates the best point to stop the roasting process with regard to the influences on oxidative beer stability. After the second reversal point a measurable over-roasting starts and an increase of prooxidative radical generation is observable again.

Altogether the described results and correlations open an innovative possibility to influence the pro-oxidative properties of roasted green malt, malt and barley by selective steering of roasting processes as well as give an partial advice for the reason of the controversially discussed pro- and antioxidative effects of roasted green malt, malt and barley and their influences on oxidative beer stability. In the range of high roasting temperatures (>220°C) the space of time including those advantageous reversal point is a very short period and make the process steering more difficult.

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