Hops and taste stability – selective hop additions for beer preservation (Part 1)

LABORATORY TESTS | It is generally known that hops are able to do much more than provide beer with bitterness, aroma and microbiological stability. To-date, the focus was on yield of bitter substances and hop aroma. However, no systematic research exists about the influence of hop addition and time of addition on oxidative beer stability. A research project at the Department of Brewing Science of the Technical University (TU) Berlin (AiF 17439) was devoted to resolving this issue.

CURRENTLY, HOP ADDITION mainly focuses on obtaining the typical bitterness of a specific beer. Hops are mostly added at the beginning of wort boiling to achieve the most intensive isomerisation possible and, thus, high yield of bitter substances. Antioxidative properties of hops are currently used only to a very limited extent and can be substantially optimised by changing hop addition. Against this backdrop, the Department of Brewing Science of TU Berlin carried out investigations in order to be able to utilise the antioxidative potential of hop addition much more selectively. Suitable worts and beer were produced on a pilot and semi-pilot scale in the Research Brewery. An important objective of the project was to minimise the level of prooxidative transition metal ions, mainly iron and copper, in finished beer by optimising and adapting hop addition. This was to show that beer with improved taste stability can be produced in this manner.

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Oxidation reactions and beer ageing

Beer and other beverages and food are subject to oxidative changes during processing, but mainly after filling or packaging. These can cause discernible off-flavours in beer. Main flavour-relevant compounds in this instance are, in particular, the aldehydes 2- and 3-methylbutanal but also methional and phenylethanal. The so-called "cardboard flavour" is introduced, resulting from trans-2-nonenal, by fatty acid oxidation. Formation of the above-mentioned aldehydes may originate from Strecker degradation and, possibly, also direct oxidation of amino acids, as has been recently demonstrated [1].

The negative role of oxygen in connection with beer ageing is generally known and undisputed. Recently, analyses based on electron spin resonance (ESR) spectroscopy made it possible to show up these oxygen-dependant reactions in a much better

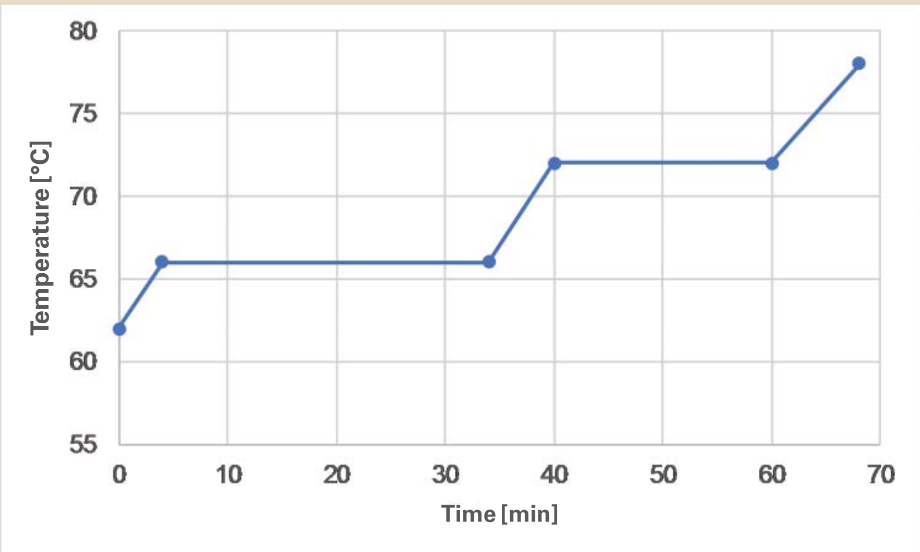

Fig. 1 High-short mashing method

manner [2]. As far as current knowledge goes, very reactive hydroxyl radicals are formed via specific activated oxygen species in the course of the metal-induced Fenton and Haber-Weiss-reaction. These ultimately react non-specifically with organic beer components. Concentration of free radicals in wort and beer generally rises in line with increasing concentrations of iron or copper and oxygen.

Recent research focussed mainly on delaying oxidative processes by taking technological measures to provide beer with a better sensory stability. When beer is brewed in accordance with the German Purity Law, addition of antioxidants such as e.g. SO_2 or ascorbic acid is strictly prohibited. It is thus possible only to keep oxygen introduction during the process low and/or minimise uptake of prooxidative components such as e.g. metal ions. A method that is in conformity with the Purity Law relates to raising the so-called endogenous antioxidative potential (EAP) of finished beer. This is possible e.g. by introduction of natural oxidation-inhibiting components in malt and hops or, by means of fermentation technology, by raising SO_2 levels formed by yeast in the course of fermentation.

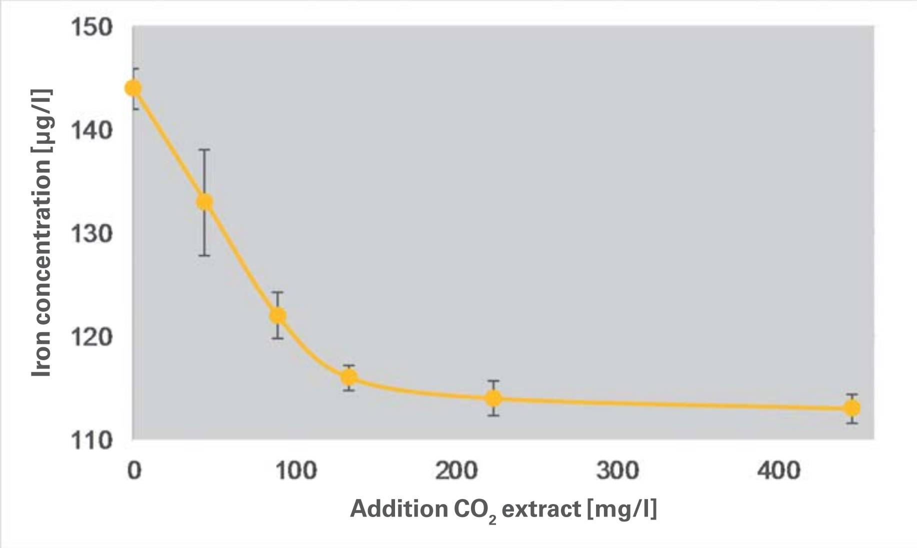

Fig. 2 Influence of hopping into mash on iron concentration (N=3)

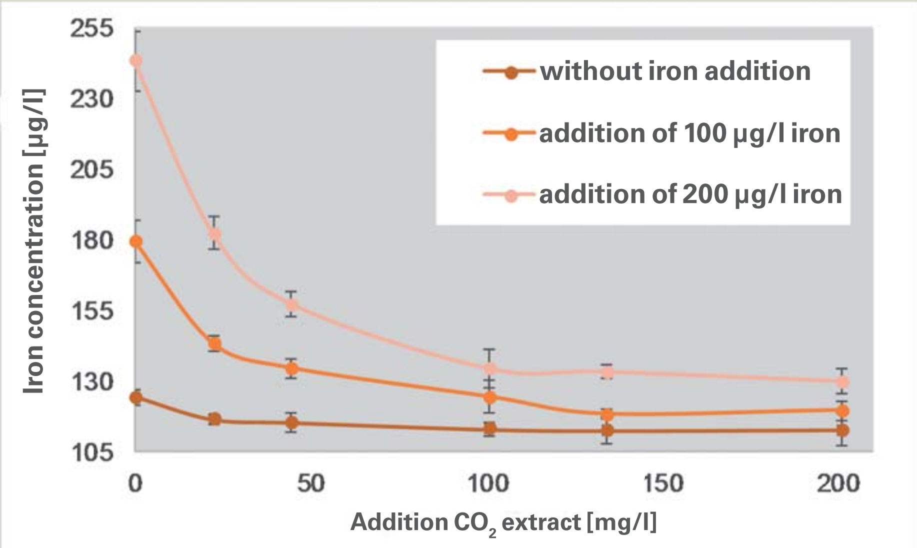

Fig. 3 Hop addition at beginning of boiling – influence on iron concentration (N=3)

Antioxidative effects of hop acids

Hops contain a multitude of antioxidative-active components. Apart from hop polyphenols described in many publications, particular attention was recently given to the antioxidative potential of hop bitter acids. Six-ring structures, such as exhibited by α- and β-acids, have demonstrably strong capabilities for inhibiting oxygen radicals [3]. Recent studies [4] show that α- and β-acids are in a position to complex prooxidative metal ions and, thus, reduce their levels during wort boiling. Though copper and iron ions were complexed by α-, β- and iso-α-acids in different ways, it was not possible to detect complexing of the metal ions calcium (Ca), potassium (P), magnesium (Mg), manganese (Mn) and zinc (Zn) [4]. The selective complexing behaviour of hop bitter acids may, thus, be regarded as favourable for beer quality as mainly prooxidative metal ions are complexed, without any negative impact on ion composition of wort and beer. Additional tests in model solutions, similar to beer wort, showed that α- and β-acids significantly counteract formation of 3-methylbutanal and 2-furfural. Iso-α-acids have no effect [5]. The effect of α-acid was thus investigated in more detail and it could be shown that, in particular, radical-induced oxidative breakdown of leucine to 3-methylbutanal was suppressed by iron(II) complexing and scavenging of radicals [5]. Antioxidative properties of hop bitter acids can be summarised as such:

- functional complexing of prooxidative transition metal ions;
- scavenging organic radicals.

It appears that inhibition of non-oxidative or oxidative paths of the Maillard reaction triggered by hop acids seems to be probable [3,5] but there is no final proof yet.

α-acids generally seem to be much more effective than iso-α-acids in terms of having an antioxidative effect. As the antioxidative potential of α-acids is "consumed", so to speak, during wort boiling as a result of isomerisation, continuous addition of α-acids during wort preparation may be advantageous in order to counter rapidly progressing oxidative processes and subsequent formation of ageing aldehydes. However, yield of bitter substances should not be disregarded. An optimised hop management would have this dual effect: high yield of bitter substances on the one hand and optimum exploitation of antioxidative properties of hop α-acids on the other hand.

Laboratory tests

To start with, tests on a laboratory scale were aimed at exploring the effectiveness of the amount of hop α-acids added or the amount of α-acid to be added to develop the

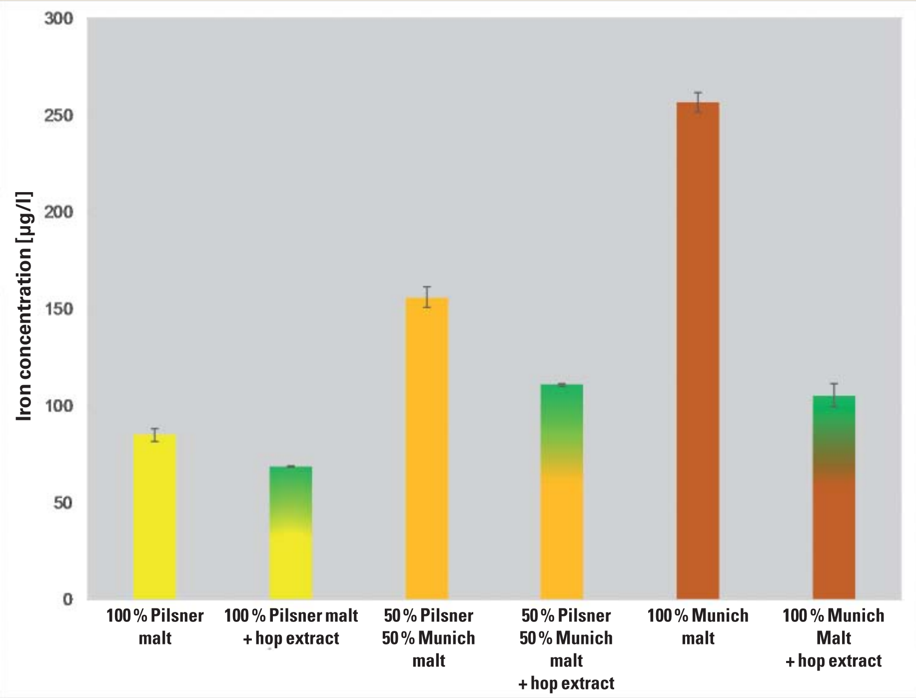

Fig. 4 Influence of malt type and hop addition on iron concentration (N=3)

ANALYSIS RESULTS OF LABORATORY WORTS (N=3)

	100 % Pilsner malt	50 % Pilsner malt, 50 % Munich malt type I	100 % Munich malt type I
Extract [w/w %]	11.80 ± 0.06	11.87 ± 0.05	11.81 ± 0.03
pH	5.70 ± 0.02	5.41 ± 0.03	5.23 ± 0.02
Colour [°EBC]	7.3 ± 0.3	18.6 ± 0.8	29.1 ± 0.4

Table 1

highest possible antioxidative effect provided by hops. The focus was on complexing prooxidative iron ions during mashing and wort boiling. The results of these preliminary tests were ultimately used as a basis for designing tests with optimised hop additions on a semi-pilot scale.

Mash hopping

Yield of bitter substances and iron precipitation during mashing was first investigated. Using a high-short mashing method (fig. 1) that was also used later on in semi-pilot tests, Pilsner malt was mashed-in in a mash bath and filtered through a pleated filter after the end of mashing. The influence of the amount of hop addition was investigated by adding 0, 20, 40, 60, 100 and 200 mg/l of hop α-acid in the form of CO_2 extract (Hallertauer Perle, c(α-acid) = 44.8 %) in the course of mashing-in. The iron concentration in worts was subsequently measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Fig. 2 shows that hop addition between 0 and 134 mg/l CO_2 extract (= 60 mg α-acid) resulted in a noticeable reduction of iron concentration of 144 µg/l in the kettle-full wort down to a concentration of 114 µg (62 %). Despite higher additions of up to 446 mg/l CO_2 extract (= 200 mg/l α-acid), this could not be pushed down further. In addition to measuring iron concentration, yield of bitter substances in the course of mash hopping was determined. This amounted to some five to six per cent in all tests and should thus be regarded as extremely unsatisfactory.

Wort boiling

In another laboratory-scale test, the influence of addition to CO_2 extract at the beginning of boiling on iron concentration in the wort was investigated. In a manner similar to that of the previous tests, a base wort was prepared using the high-short mashing method. Worts were heated until start of boiling and 100 and 200 µg/l iron(II) respectively were added to obtain different iron concentrations in the wort. A control wort without iron addition was also prepared. 0, 10, 20, 45, 60 and 90 mg/l α-acid were subsequently added in form of CO_2 extract. The iron content was subsequently determined again using ICP-OES.

Similar to mash hopping, a maximum reduction of iron from 100 to 134 mg/l CO_2 extract (= 45-60 mg/l α-acid) was observed (fig. 3). It is noteworthy that only 55 to 60 % of additions of iron of 100 to 200 µg/l were recovered in the worts. This may be attributable to the fact that iron reacts with substances in the worts, such as e.g. polyphenols that have free bonding sites, and are converted into non-soluble complexes.

Influence of malt type and hop addition

The influence of malt type on iron concentration in the wort was subsequently investigated. Kettle-full wort was again prepared on a laboratory scale. Three batches were prepared:

I. 100 Pilsner malt;
II. 50 % Pilsner malt, 50 % Munich malt type I;
III. 100 % Munich malt type I.

The worts were subsequently heated using a reflux condenser until beginning of boiling. At the beginning of boiling, hops were added, having 100 mg/l α-acid (CO_2 extract Hallertauer Magnum, c(α-acid = 47.9 %) in each instance. Extract, pH and colour of worts were determined in addition to iron concentration.

Extract contents fluctuated to a limited extent. The pH value dropped considerably, when the percentage of Munich malt type I was increased. As had been expected, colour values rose considerably when the amounts of hop addition were increased.

Fig. 4 is a bar diagram of iron concentrations. The composition of grists had an unequivocal effect on iron concentration in worts. Analogous to colour values, it rose in line with higher percentage additions of Munich malt type I. Hopping in turn clearly lowered iron concentration. Depending on malt or malt mix used, hop addition resulted in precipitation of more or less iron in percentage points. When adding 100 % Pilsner malt, iron concentration in worts was 19 % lower compared to the control without hopping. When using a blend of Pilsner malt and Munich malt type I in equal proportions, it dropped by 29 %, and even by 59 % when adding 100 % Munich malt type I. It may be the case that iron is released from its bonded form to a greater extent when adding Munich malt that is subjected to more intensive kilning, so that hop addition in turn results in precipitation of a higher percentage of total iron. This phenomenon cannot yet be explained adequately with current scientific knowledge. The influence of malt on oxidative beer stability and iron concentrations is currently investigated in detail in another research project at the Department of Brewing Science of the TU Berlin (AiF 17641).

Summary

In summary, data measured indicate that the effect of hop addition shows a clear-cut dependency of both the malt added and the wort matrix. Accordingly, hop addition should always be adapted to malt and wort composition so as to achieve the highest possible precipitation of iron and, thus, maximum complexing and/or precipitation of prooxidative metal ions as early as possible in the course of wort preparation. Maximum possible precipitation of iron ions should initially be determined in laboratory tests in order to use such data as a basis for optimising hop addition. Research is currently ongoing in this respect at the TU Berlin in order to be able to formulate general rules for different malt mixes and hopping additions. In the context of the results of these tests and under the conditions described, addition of 45-60 mg/l hop α-acids during mashing and at the beginning of boiling optimised iron precipitation. Data gathered in laboratory tests was the basis for designing tests on a semi-pilot scale. Part 2 of this article will describe the test procedure and results of optimised hop additions. ■

Literature

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