Hops and taste stability – selective hop additions for beer preservation (Part 2)

PILOT TESTS | Part 1 of this contribution (see BRAUWELT International No. 2, 2019, pp. 144-147) reported about tests with mash and wort on a laboratory scale in which precipitation of prooxidative iron ions using hop α-acids in the form of CO_2 extract additions was investigated. Part 2 deals with optimised hopping in order to trigger systematic precipitation of hop irons during brewing and thus extend the shelf life of beer.

FINDINGS REPORTED IN PART 1 of this technical contribution showed that malt and wort composition has a major influence on the effectiveness of hop addition in terms of precipitation of iron ions. The malt used, in particular, seems to have major influence on the iron concentration of the wort and on accessibility of iron for complexing with hop α-acids. Addition of CO_2 extract of 45-60 mg/l was found to be optimal for iron precipitation in the case of mash hopping and additions at the beginning of wort boiling in the laboratory tests. This data was used for planning optimised hop additions on a pilot scale.

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Authors: Dr. Philip Wietstock (l.), Thomas Kunz (r.) and Prof. Frank-Jürgen Methner, Chair of Brewing Science, Berlin Institute of Technology, Berlin, Germany

Pilot test procedure

Two simultaneous test series on a semi-technical scale of two hectolitres were carried out. Malt grist consisted of 90 % Pilsner malt and 10 % Munich type I malt. An original gravity of around 12 °P was the target. As in the first part of this contribution, a high-short process was used for mashing. Hop additions were exclusively with CO_2 extract of Hallertauer Magnum (c(α-acid)=47.9 %). These were adapted based on the results of the laboratory tests (see table 1). The first hop addition was chosen such that maximum precipitation of iron ions could be achieved. Moreover, the various hop additions should cover the widest spectrum possible in order to be able to subsequently map the effect in terms of analytical beer parameters, sensory parameters and oxidative beer stability. For mash hopping, hops were added at the beginning of mashing-in. For first wort hopping, they were added at the beginning of lautering. A reference brew was prepared with only one hop addition at the beginning of boiling. Hopping of the test brews was varied individually to obtain similar bitterness in the finished beers. The percentage values in brackets in table 1 show the quantities added, compared to the reference brew. Each wort was boiled at atmospheric pressure for 60 minutes. Yeast strain W 34/70 was used for pressureless fermentation at 14 °C. After a warm day at ambient temperature and subsequent storage for four weeks at 0-2 °C, the beers were filtered using a three-stage membrane filtration process and filled in 0.5 l containers. The oxygen value measured after filling was < 50 µg/l. After filling, the beers were stored for twelve weeks at 28 °C. The level of staling aldehydes was subsequently determined and a sensory analysis in accordance with DLG carried out.

Analysis of pilot tests

The fresh beers were analysed after filling in order to be able to improve characterisation of the influence of hop additions. Unless stated otherwise, analyses were carried out according to Mebak. Hop bitter acid values of the beers were analysed using HPLC according to the ASBC method Beer 23.C. SO_2 levels of beers were measured using flow injection analysis in accordance with the specifications of a method optimised at the Department of Brewing Science of the TU Berlin [1, Mebak 2.21.8.3]. As in the first part of this contribution, iron levels were determined using ICP-OES.

Table 2 lists the analytical beer data of the test brews. It can be concluded from the data that the modified hop additions did not have any negative impact on the standard analysis parameters measured and that all parameters were within a normal range for beers of the Pilsener type.

Iso-α-acid levels of the beers produced with split hop addition (SHA), first wort hopping (FWH) or continuous hopping (COH) were slightly lower compared to the reference whereas the beer produced with mash hopping (MAH) had slightly higher ones. As had been expected, α-acid and β-acid levels were very low. This can be attributed to precipitation of α-acid during fermentation and storage induced by pH

HOP ADDITIONS IN PILOT TESTS

Brew designation	Acronym	Addition of α-acids: Mashing-in	First wort	Beginning of boiling	Mid-time of boiling	End of boiling	Whirlpool
Reference brew (100%)	REF	–	–	90 mg/l	–	–	–
Mash hopping (156%)	MAH	60 mg/l	–	81 mg/l	–	–	–
Split hop addition (110%)	SHA	–	–	45 mg/l	27 mg/l	18 mg/l	9 mg/l
First wort hopping (100%)	FWH	–	45 mg/l	–	27 mg/l	18 mg/l	–
Continuous hopping (100%)	CON	–	–	45 mg/l	10*4.5 mg/l every 5 min	–	

Table 1

ANALYSIS DATA OF PILOT BEERS PRODUCED

		First brew series					Second brew series				
		REF	MAH	SHA	FWH	CON	REF	MAH	SHA	FWH	CON
Original gravity	[% by wt]	11.27	11.41	10.94	11.36	11.12	11.14	10.89	11.11	11.21	11.08
E_s	[% by wt]	1.83	1.90	2.01	2.06	1.96	2.31	2.03	1.99	1.97	1.95
Alc.	[% by vol]	4.99	5.03	4.71	4.92	4.84	4.67	4,68	4.82	4.88	4.82
V_s	[%]	83.7	83.3	81.6	81.8	82.4	79.2	81.4	82.1	82.4	82.4
Colour	[EBC]	6.8	6.7	7.1	6.8	6.4	6.9	7.0	7.4	8.0	7.4
pH	-	4.40	4.37	4.31	4.41	4.35	4.30	4.33	4.35	4.37	4.33
Total N (12 %)	[mg/l]	738	667	671	631	694	717	733	770	808	724
FAN (12 %)	[mg/l]	79	82	58	81	72	73	75	89	90	72
Polyphenols (12 %)	[mg/l]	149	154	141	145	144	152	149	156	157	145
Iso-α-acid	[mg/l]	24.4	26.2	18.0	20.6	21.6	22.9	20.3	16.9	19.5	21.3
α-acid	[mg/l]	<1	1.0	<1	2.3	<1	<1	<1	<1	1.1	<1
β-acid	[mg/l]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bitterness units	[BU]	26	27	18	22	22	23	22	19	22	22
Yield of bitter substances	[%]	29.9	19.1	18.2	24.4	24.4	25.6	15.6	19.2	24.4	24.4
SO_2	[mg/l]	4.2	3,9	3.5	3.8	3.5	4.4	3.2	4.7	3.4	3.2
Iron	[µg/l]	77	56	56	69	51	74	56	53	64	54
EAP-value	[min]	211	200	185	191	186	231	181	216	152	171
T_{600}-value [*10^6]	[-]	0.85	0.65	0.66	0.99	0.61	0.64	0.64	0.67	1.13	0.83

Table 2

and temperature. In contrast to the pitching worts, bitterness units – analogous to the iso-α-acid levels – were also slightly lower compared to the reference, except for the MAH sample from brew series 1.

Iron content of all test brews was always lower compared to the reference, in some instances up to 28 %. This can be regarded as clear evidence for the positive effect of hopping on precipitation of prooxidative iron ions. The occurrence and amount of oxygen radicals in the finished beers was determined using electron-spin resonance (ESR) spectroscopy. It was obvious that the lower iron values were clearly reflected by the T_{600} values (maximum amount of radicals generated). As a result of modified hop additions, concentrations of oxygen radicals measured using ESR were lower. Beers produced with first wort hop addition were an exception: despite lower iron contents, the T_{600} levels measured were higher. Increased formation of radicals in the FWH beers cannot yet be explained plausibly based on data available and state-of-the-art.

SO_2 levels of the brews ranged from 3.2-4.4 mg/l. These differences are attributable to fermentation but have to be taken into account when considering and interpreting the ESR results. When the SO_2 level is high, the endogenous antioxidative potential (EAP) is generally also higher. However, this cannot be ascribed to modified hop additions but it is related to fermentation, as already mentioned. Thus, the EAP values of the fresh beers correlated with the SO_2 levels and, analogous to the SO_2 levels, were very similar. An alternative measurement method for determining oxidative stability independently of the SO_2 level is the so-called "Beverage Antioxidative Index" (BAX) [2]. This value was not analysed in the context of the tests. However, an approximate value is obtained when dividing the EAP value of a sample by the SO_2 value.

Analytical determination of the BAX value and its detailed functional principle has been described extensively in the past

[2]. The BAX value indicates the influence of the beer matrix on SO_2 consumption as a result of wort and beer components having an oxidative effect. The higher the BAX value, the longer it will take until the SO_2 is depleted during storage and the beer will exhibit higher taste and haze stability. When applying this relationship to the samples, a first approximation of the BAX values would be 50.2 - 53.1 min*mg^{-1}*l in brew series 1 und 45.9 - 56.6 min*mg^{-1}*l in brew series 2. With the exception of first wort hopping of test series 2, the calculated BAX value in the reference worts was lowest, clearly indicating increased oxidative stability as a result of modified hop additions.

Aldehyde levels of pilot beers

Following storage for twelve weeks at 28 °C in the dark, beer staling aldehydes were determined using Solvent-Assisted-Flavor-Evaporation(SAFE)-GC/MS [3]. Staling aldehydes of the fresh reference beers were also measured for comparison.

In both test series, the sum of staling aldehydes increased during storage as compared to the fresh reference (table 3). The level of staling aldehydes in test series 2 was slightly lower than in test series 1. But it is quite obvious that similar trends are likely to emerge compared to the corresponding reference beers. Following forced storage, the reference beers (REF) had the highest level of oxidation indicators 2- and 3-methylbutanal, methional and phenylethanal as well as thermal indicator substances 2-furfural. The level of the other aldehydes rose only slightly during storage. However, no clear-cut influence of hopping could be determined again but these other aldehydes are not relevant in sensory terms.

The beers produced with mash hopping had very low levels of staling aldehydes. Only the split hop addition in brew series 2 had slightly lower values than the corresponding MAH beer. In some instances, the aldehyde levels of mash hopped beers after a storage period of twelve weeks was even below the aldehyde level of the fresh reference beers. The positive effect of mash hopping can presumably be ascribed to the fact that oxidative processes are minimised by hop addition in the course of mashing and, thus, oxidation of beer components and formation of staling aldehydes is prevented. 2-furfural, usually an indicator for thermal stress of a sample, was also influenced by the way hops were added. This coincides with recently published results by Wietstock et al. [4] and thus questions the significance of this parameter as just a thermal indicator of a sample. As far as the tests described here are concerned, e.g. the thermal stress of two samples produced with different hop additions can be compared only to a limited degree using the 2-furfural indicator.

When looking at the sum of all aldehydes and compare it to the reference tests, it is apparent that only modification of hop addition reduces these compounds by 43.9-66.9 % (brew series 1) and by 48.7 - 60.9 % (brew series 2). Optimised hop addition can be regarded as a measure for suppressing staling aldehydes and thus the progress of staling without any doubt.

DLG tasting results

In order to validate analytical results, both the fresh as well as forced aged beers were tasted in accordance with the DLG regime. Results are shown in Table 4. Fresh beers

STALING ALDEHYDES OF FRESH REFERENCE BEERS AND AGED BEERS IN µG/L

			Forced aged beers (12 weeks, 28 °C)				
		REF (fresh)	REF	MAH	SHA	FWH	CON
Brew series 1	3-methyalbutanal	5.0	14.0	4.0	9.4	13.0	5.5
	2-methylbutanal	2.9	9.3	3.4	5.7	8.0	4.7
	2-furfural	1.7	53.0	18.0	12.0	18.0	14.0
	Methional	2.3	9.5	2.3	7.2	5.9	6.5
	Benzaldehyde	< 1.0	1.4	< 1.0	< 1.0	1.3	< 1.0
	Phenylethanal	2.6	5.3	2.4	3.1	4.8	3.3
	Nicotic acid ethyl ester	3.2	7.4	6.2	3.6	9.3	3.7
	γ-nonalactone	6.1	16.1	14.6	13.3	17.3	15.0
	Σ aldehydes	23.8	116.0	50.9	54.3	77.6	52.7
Brew series 2	3-methyalbutanal	3.9	9.6	2.4	4.3	6.5	5.8
	2-methylbutanal	2.4	6.2	1.9	3.4	5.1	4.8
	2-furfural	2.0	44.0	14.9	12.8	18.7	16.0
	Methional	2.5	8.8	3.8	4.3	5.8	4.7
	Benzaldehyde	< 1.0	1.3	1.0	1.3	1.1	1.1
	Phenylethanal	1.9	3.9	3.3	4.1	4.0	3.5
	Nicotic acid ethyl ester	2.8	5.6	9.1	4.9	6.7	4.5
	γ-nonalactone	5.8	15.5	12.8	11.1	9.9	13.0
	Σ aldehydes	21.3	94.3	49.2	46.2	57.8	53.4

Table 3

DLG TASTING RESULTS OF FRESH AND FORCED AGED PILOT BEERS

		Fresh beers					Forced aged beers				
		REF	MAH	SHA	FWH	CON	REF	MAH	SHA	FWH	C
Brew series 1	Purity of smell	4.6	5.0	4.8	5.0	5.0	3.2	4.3	4.2	4.1	4.2
	Purity of taste	4.5	5.0	4.0	4.7	4.6	3.2	4.4	4.5	4.3	4.3
	Body	4.6	4.6	4.0	5.0	4.8	4.4	4.5	4.2	4.5	3.6
	Carbonation	4.6	5.0	4.4	4.4	5.0	4.3	4.7	4.5	4.6	4.4
	Quality of bitterness	4.0	4.4	4.0	4.4	4.7	3.2	4.5	4.3	4.0	4.6
Brew series 2	Purity of smell	3.2	4.3	4.2	4.1	4.2	3.7	3.3	4.4	4.3	4.3
	Purity of taste	3.2	4.4	4.5	4.3	4.3	3.8	3.1	4.1	4.1	4.4
	Body	4.4	4.5	4.2	4.5	3.6	4.0	4.0	4.0	4.3	4.0
	Carbonation	4.3	4.7	4.5	4.6	4.4	4.3	4.1	4.4	4.6	4.6
	Quality of bitterness	3.2	4.5	4.3	4.0	4.6	4.0	4.0	3.9	3.9	4.0

Table 4

were not awarded inferior scores. After the storage period, the reference beer of brew series 1 received clearly inferior scores for the attributes "purity of taste" and "purity of smell". This would ultimately mean that this beer would be classified as no longer being saleable. The panel unambiguously described these beers as "oxidised". Though the beers with modified hop addition were also downgraded after storage compared with the fresh beers, the difference was clearly smaller. The fresh beers from brew series 2 were also awarded scores between 4.2 and 4.8 for the attributes purity of taste and purity of smell. As far as the other tasting attributes were concerned, no beer was downgraded. The forced aged beers REF and MAH received clearly inferior scores. The beer REF was described as "oxidised". In the case of the MAH beer, the reason for downgrading could not be identified because, analogous to the first brew series, aldehyde levels were very low and the panel did not indicate any other shortcomings. This notwithstanding, it is obvious that beers SHA, FWH and CON were classified as still being saleable und, analogous to brew series 1, clearly differ from the reference.

Summary

The tests unambiguously suggest that modified hopping results in a clear increase in oxidative stability and thus in minimising formation of staling aldehydes after a storage period of twelve weeks at 28 °C. Based on results obtained, this effect is mainly due to functional precipitation of prooxidative iron ions by hop bitter substances in the course of the brewing process and associated minimisation of oxidative reactions. It can also not be excluded that other mechanisms of action such as scavenging organic radicals or

inhibition of certain paths of the Maillard reaction also play a part. It should be taken into account that the percentage split of hop additions has to be adapted to the hop matrix to achieve the highest possible effect. Depending on the type of hopping, higher amounts of hops have to be added in order to obtain the same bitterness in the finished beers. Increased hop addition may be regarded as helpful if it leads to a clearly higher oxidative stability. Continuous hopping seems to be the most practicable solution because bitter substance yield is just slightly reduced compared to the reference thought the beers had a clearly higher oxidative stability, both in analytical and sensory terms.

Lüder's [5] statement published in 1950 that modified hop additions are "considerable wastefulness" seems to apply in terms of bitter substance yield but mash hopping turned out to be indeed a positive measure for suppressing staling aldehydes during storage. ■

Literature

1 Kunz, T.; Schiwek, V.; Harms, D.: "Optimized analysis methods for the determination of SO_2 in beer and malt", in: BRAUWELT International, No. 4, 2009, pp. 216-220.

2 Kunz, T.; Müller, C.; Methner, F.-J.: "EAP Determination and Beverage Antioxidative Index (BAX) – Advantageous Tools for Evaluation of the Oxidative Flavour Stability of Beer and Beverages (Part 1)", in: BrewingScience, No. 1-2, vol. 66, 2013, pp. 12-22.

3 Engel, W.; Bahr, W.; Schieberle, P.: "Solvent assisted flavor evaporation – a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices", in: European Food Research and Technology, vol. 209, 1999, pp. 237-241.

4 Wietstock, P. C.; Baldus, M.; Öhlschläger, M.; Methner, F.-J.: "Hop Constituents Suppress the Formation of 3-Methylbutanal and 2-Furfural in Wort-Like Model Solutions", in: Journal of the American Society of Brewing Chemists, No. 1, vol. 75, 2017, pp. 41-51.

5 Lüers, H.: "Die wissenschaftlichen Grundlagen von Mälzerei und Brauerei", Fachverlag Hans Carl GmbH, Nuremberg, 1950.