EFFECT OF STORAGE DURATION AND ATMOSPHERE ON THE CONTENT AND PRICE OF HOP ALPHA BITTER ACIDS*

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The quality of hops is significantly affected by the content of alpha bitter acids. Maintaining it with minimum losses lies within the competence of both the hop grower and processor depending on how they follow the optimum harvest technology, storage conditions, and post-harvest hop processing. That indicator is considerably affected by the hop storage method, i.e. whether the warehouse is air-conditioned or not, as well as the storage duration. The alpha bitter acid content should not be reduced during storage. The objective of this paper is an analysis of the alpha bitter acid content in the Saaz hop variety in a technological sequence of operations starting with drying at the grower and finishing with six-month storing at the processor, with three storage variants: an air-conditioned warehouse, non-conditioned warehouse, and a variant in which the square bale is moved after 60 days from a non-conditioned warehouse into an air-conditioned warehouse. The analysis of samples to identify the alpha bitter acid content was carried out by means of the ASBC Hops-6 and the HPLC EBC 7.7 methods. Practically in all cases the alpha content declines, although if a square bale is placed in an air-conditioned warehouse this decline is the lowest depending on the storage duration. The economic analysis shows a significant profit referring to the price of alpha contained in 1 t of hops stored in an air-conditioned warehouse. At the date of 1/11/2015 this profit was 14 706 CZK, at the date of 4/1/2016 it was 7646 CZK, and at 1/3/2016 the profit was 6587 CZK.

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INTRODUCTION

Nowadays, a considerable attention is given to the evaluation of quality of agricultural products as the basic raw materials for food production. The same applies to hops, although they are not a direct food raw material. The hop quality is evaluated already when dispatched at the grower, then at the hop processor prior to their distribution to purchasers, and finally in domestic and foreign breweries (George, Bryant, 2001; Kumhala et al., 2013).

The alpha bitter acids content is a parameter that significantly influences the quality and price of hops. It is a component of hop resins modifying considerably the so-called hop brewing value, i.e. the value of bitterness. Its maintaining with minimum losses lies within the competence of both the hop grower and the processor depending on how consistently they follow the entire technological process including the finalization of the hop product (Rybacek et al., 1980; Krofta, Rybka, 2015).

The afore mentioned indicator is already significantly affected by the process of hops preservation by drying in the stationary processing line of the grower during which the water content in hop cones reduces from the initial approximately 80% to 8 or 10% (Srivastava et al., 2006; Jech et al., 2011; Kumhala et al., 2016). Another important factor

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Table 1. Average values of the alpha bitter acids content of hops under different storage conditions

Hops variety	Alpha bitter acids content (%)										
	After the picking line		Before pressing		Storage	1/11/2015		4/1/2016		1/3/2016	
	ASBC Hops-6	HPLC EBC 7.7	ASBC Hops-6	HPLC EBC 7.7		ASBC Hops-6	HPLC EBC 7.7	ASBC Hops-6	HPLC EBC 7.7	ASBC Hops-6	HPLC EBC 7.7
SH	3.46	2.91	3.08	2.90	N	2.89	2.65	2.56	2.72	2.45	2.52
					N/K	2.99	2.76	2.62	2.73	2.53	2.56
					K	3.09	2.88	2.70	2.81	2.58	2.59

ABSC Hops-6, HPLC EBC 7.7 = methods determining the alpha bitter acids content in hops,

SH = Saaz hop variety, N = non-conditioned warehouse, N/K = 60 days after pressing non-conditioned warehouse, then air-conditioned warehouse, K = air-conditioned warehouse

affecting hop qualitative indicators is the storage method (Doe, Menary, 1979). After having been pressed into square bales at the grower the hops are usually dispatched to the warehouse of the processor where they are gradually processed which is usually staggered over a period of up to half a year after the harvest. A significant role is hence played by the storage duration and method followed by the processor, whether the warehouse is air-conditioned or not.

The objective of this paper was to analyze the alpha bitter acid content in the technological sequence of operations starting with drying at the grower and finishing with a six-month storing at the processor under variant storage conditions. The alpha bitter acid content is the most important qualitative parameter of hops that can be determined in a variety of ways.

MATERIAL AND METHODS

The measurement focused on the hop variety Saaz, the most widespread variety in the Czech Republic (87% of hop acreage).

For the purpose of laboratory analyses detecting the alpha bitter acid content, samples were taken at the hop grower (CHMEL-Vent Co. Ltd. Kněžice, Czech Republic) after passing the hop-picking line (before entering the dryer) and after hop drying before pressing, and at the hop processor (Chmelařství, cooperative Žatec, Czech Republic) for three variants of storage and in three terms each time after a two-month storage.

As concerns the sampling at the hop grower (on 29/8/2015), after passing the picking line (before entering the dryer), 3 samplings were carried out at 2-hour intervals (at 7, 9, and 11 h) and from each sampling 3 samples were taken to be analysed. From the same hops batch, after being dried and before being pressed, 3 samplings were carried out at 2-hour intervals (at 17, 19, and 21 h) and from each sampling 3 samples were taken to be analysed.

Concerning the sampling at the hop processor, from the same batch, on which the samples at the grower had been collected 3 square bales were put aside and one by one used for 3 storage variants immediately after pressing. One square bale was placed into an air-conditioned warehouse (K), the second into a non-conditioned warehouse (N), and the third was placed into an air-conditioned warehouse (N/K) 60 days after being pressed (from being pressed for up to 60 days it was placed into a non-conditioned warehouse). With each square bale always 1 sampling was performed at 2-month intervals (on 1/11/2015, 4/1/2016, and 1/3/2016) and 3 samples were taken from each sampling for the purpose of the analysis.

The samples analysis detecting the content of alpha bitter acids was performed using the ASBC Hops-6 method in the laboratory of Chmelařství, cooperative Žatec, Czech Republic. For each sampling place 1 composite sample was evaluated for comparative purposes to determine the content of alpha bitter acids following the HPLC EBC 7.7 method (Claus et al., 1978; Forster, 1987; Green, Osborne, 1993).

The alpha bitter acid content was determined through liquid chromatography HPLC column

Nucleosil 100-5 C18, 250/4 mm (Macherey-Nagel, Germany) when the alpha bitter acids were extracted by means of diethyl ether-methanol mixed with diluted solution of hydrochloric acid. To quantify the alpha bitter acids, an external standard (ICE 3) was used, the composition of which is verified regularly through international ring tests (Ono et al., 1984; Hermans-Lokkerbol, Verpoorte, 1994).

The number of samples for laboratory analysis totalled 56, out of which 45 were subjected to the ASBC Hops-6 analysing method and 11 composite samples were subjected to the HPLC EBC 7.7 analyzing method. The ASBC Hops-6 analyzing method included 9 samples after passing the picking line, 9 samples before pressing, and 27 samples from the stored square bales (3 warehouses x 3 samplings x 3 samples). The HPLC EBC 7.7 analyzing method covered 1 composite sample after passing the picking line, 1 composite sample before pressing and 9 composite samples taken from the stored square bales (3 warehouses x 3 samplings x 3 samples).

The air temperature and relative humidity on individual belts of the belt dryer were measured on the sampling day by means of COMET sensors T3419 (COMET SYSTEM Co. Ltd. Rožnov pod Radhoštěm, Czech Republic) every hour between 8 and 21 h.

Table 2. Temperature and relative humidity of the drying air

Drying belt	Temperature range (°C)	Relative humidity range (%)
1	41.1–45.0	25.1–30.8
2	48.0–52.9	13.3–17.0
3	53.9–57.9	7.7–15.8

RESULTS

Sampling and laboratory analyses consistently followed the selected methodology. Prior to the samplings as such, technical maturity of the harvested hops had been assessed. The cone colour was bright yellow-green with a natural shine, the vast majority of the cones were closed and flexible when squeezed, the scent was distinct and typical for this particular variety. Lupulin was bright lemon-yellow in colour, representation of biological impurities (leaves, parts of hop bines, leafstalks) was proportionate, and there were no biological impurities (Likens et al., 1970; Hanousek et al., 2008). The laboratory measurement results are tabulated and arranged in graphs in Fig. 1 and 2.

Table 1 offers the average values reflecting the content of alpha bitter acids in the technological process of monitoring the quality of the Saaz hop variety including its distinct storage method. The alpha bitter acids content was monitored by means of two different methods (ASBC Hops-6 and HPLC EBC 7.7).

The data referring to the alpha bitter acid content for the Saaz hop variety in Table 1 at the place designated as 'After the picking line' and 'Before pressing' (ASBC Hops-6 method) represent the averages of nine values (3 samples per 3 samplings). As regards the square bales in individual warehouses and given time sequence, it is the average of three values of the alpha bitter acid content. Regarding the alpha bitter acid content in the Saaz hop variety determined by the HPLC EBC 7.7 method, at each sampling place the data is based on only one value obtained from the composite sample.

Alpha bitter acids

Fig. 1 illustrates the course of changes in the alpha bitter acid content, starting at the end of the picking line and finishing approximately half a year after harvest (on 1/3/2016), for three different storage variants. The alpha content was determined by the ASBC Hops-6 method, suitable especially for fresh hops (Henderson, Miller, 1972). Desirable is the lowest possible decrease in the alpha value in the course of storing at the hop processor (Krofta, 2008). The graph builds on the average values presented in Table 1. The standard deviation characterizing variance around the average values was very low and for each sampling it did not exceed the range of 0.0081-0.1819%. The standard deviation was always determined from the alpha results at the same sampling dates and points.

Fig. 2 shows a similar graph but this time the HPLC EBC 7.7 method was used for the alpha content determination. It is a more expensive, yet more accurate method for determining the alpha content, enabling to determine it even in older hops. Similarly, the lowest possible decrease in the alpha content is also desirable in the course of storing at the hop processor. At each sampling point we built on only one value obtained from the composite sample.

Air temperature and relative humidity on individual belts of the belt dryer

After the regime stabilization (after 10 a.m.), the full-day measurement (8 – 21 h) concluded that the values of air temperature and relative humidity showed only minimum variations (Table 2).

The air temperature and relative humidity ranges on individual belts have a logical inter-relation – the temperature gradually rises from the first to the third belt, whereas the relative humidity decreases.

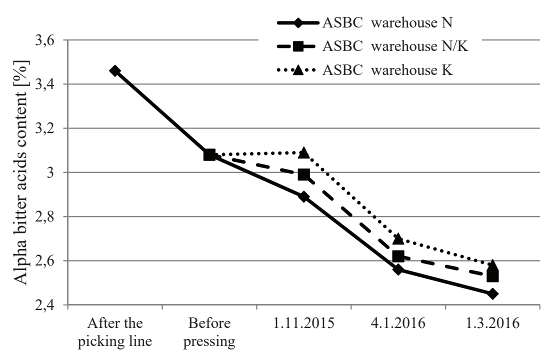


Fig. 1. Alpha bitter acids content determined by the ASBC Hops-6 method

Table 3. Storage capacity and occupancy, alpha weight and price

Parameter	Product/method	Unit	Value
Storage capacity	hop moisture of 10%	t	1 500
Storage capacity	dry hops	t	1 350
80% warehouse occupancy	hop moisture of 10%	t	1 200
80% warehouse occupancy	dry hops	t	1 080
Price	hop moisture of 10%	CZK t^{-1}	190 000
Price	dry hops	CZK t^{-1}	211 111
Price in the warehouse (80%)		CZK	227 999 880
Alpha content before pressing	ASBC Hops-6	%	3.08
	HPLC EBC 7.7	%	2.90
	average	%	2.99
Alpha weight		kg t^{-1}	29.90
Alpha price		CZK kg^{-1}	7 061

DISCUSSION

Long-time monitoring of the alpha bitter acid content in the Saaz hop variety as well as in other hybrid hop varieties grown in the Czech Republic shows a great variability influenced by variety, soil, and climatic conditions. The measurements made are the initial monitoring of changes in the alpha content under different storage conditions. There is an assumption that similar measurements will be repeated in the following years so that the measured values courses could be analyzed in a more precise way. It is practically impossible to make the experiment results a subject of discussion with foreign sources, as the results of similar measurements conducted in countries with hop growing tradition are not available.

The analysis of lupulin glands gave results for different varieties for the main quality indicators used by hops producers. The effect of storage on hop quality however was not tracked (Killeen et al., 2017).

In domestic literature only one source of information addressing a similar subject has been found (Krofta et al., 2013). The effect of storage on hop quality was monitored for the hybrid variety of Vital which is only partially comparable with the most wide-spread Saaz hop variety. The content of alpha was detected by means of HPLC EBC 7.7 method, in the same way as with the Saaz hop variety. After a year of storage in a non-conditioned warehouse, the loss in alpha for Vital ranges from 22.4 to 34.6%, while for the Saaz hop variety the alpha loss after a half-year storage reaches 13.1%. In a conditioned warehouse, the alpha loss for Vital after one year of storage ranges between 3.8 and 5.9%, whereas with the Saaz hop variety after a half-year storage the loss of alpha is 10.7%. With the non-conditioned warehouse the data reflecting loss in alpha for both varieties due to storage are relatively comparable, whereas with the conditioned warehouse the loss in alpha with the Saaz hop variety is significantly higher in percentage in comparison with Vital.

Fig. 2. Alpha bitter acids content determined by the HPLC EBC 7.7 method

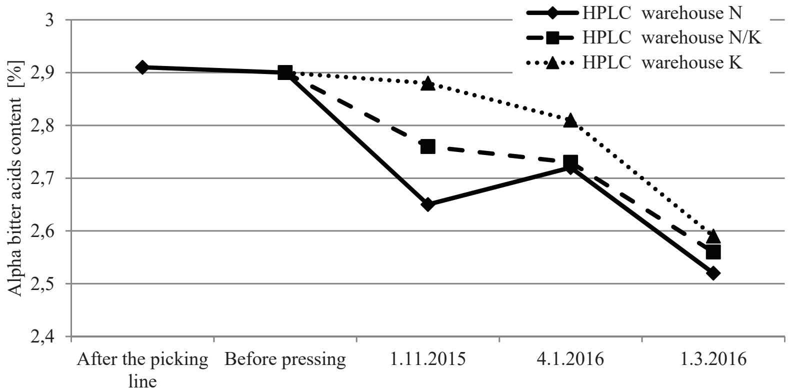


Table 4. Alpha weight and price in different storage conditions

Warehouse	Parameter	Unit	1/11/2015	4/1/2016	1/3/2016
K	ASBC Hops-6	%	3.09	2.70	2.58
	HPLC EBC 7.7	%	2.88	2.81	2.59
	average	%	2.98	2.75	2.58
	alpha weight	kg t^{-1}	29.85	27.55	25.85
	decline in alpha weight	kg t^{-1}	0.05	2.35	4.05
	decline in alpha price	CZK t^{-1}	353	16 592	28 595
	decline in price of alpha in storage (80%)	CZK	476 589	22 399 666	38 603 679
N/K	ASBC Hops-6	%	2.99	2.62	2.53
	HPLC EBC 7.7	%	2.76	2.73	2.56
	average	%	2.87	2.67	2.54
	alpha weight	kg t^{-1}	28.75	26.75	25.45
	decline in alpha weight	kg t^{-1}	1.15	3.15	4.45
	decline in alpha price	CZK t^{-1}	8 120	22 241	31 420
	decline in price of alpha in storage (80%)	CZK	10 961 538	30 025 084	42 416 388
N	ASBC Hops-6	%	2.89	2.56	2.45
	HPLC EBC 7.7	%	2.65	2.72	2.52
	average	%	2.77	2.64	2.48
	alpha weight	kg t^{-1}	27.70	26.40	24.85
	decline in alpha weight	kg t^{-1}	2.20	3.50	5.05
	decline in alpha price	CZK t^{-1}	15 533	24 712	35 656
	decline in price of alpha in storage (80%)	CZK	20 969 900	33 361 204	48 135 452

ABSC Hops-6, HPLC EBC 7.7 = methods determining the alpha bitter acids content in hops

As mentioned above, a considerable variability in variety, soil and, climatic conditions is reflected, but a decline in alpha depending on storage time is clearly visible especially in the non-conditioned warehouse.

When comparing graphs in Fig. 1 and 2, it is more appropriate to concentrate on the alpha courses from the end of hop drying (before baling) over the period of half a year of storage under different conditions. The trend in alpha content reduction is obvious using both measuring methods. The alpha courses clearly demonstrate that an air-conditioned warehouse is more suitable for hop storage.

The presented course of changes in the hops alpha bitter acids content was subjected to an economic analysis. We built on the storage capacity and the average occupancy with the Saaz hop variety. The storage occupancy was about 80%, the remaining part was evenly filled with Sládek and Premiant varieties. The price for 1 t of harvested hops is based on the average of prices in 2015. Other data are related to the alpha content values determined before pressing at the grower (Table 3). Distinction in the alpha content with different storage methods is clear from Table 4.

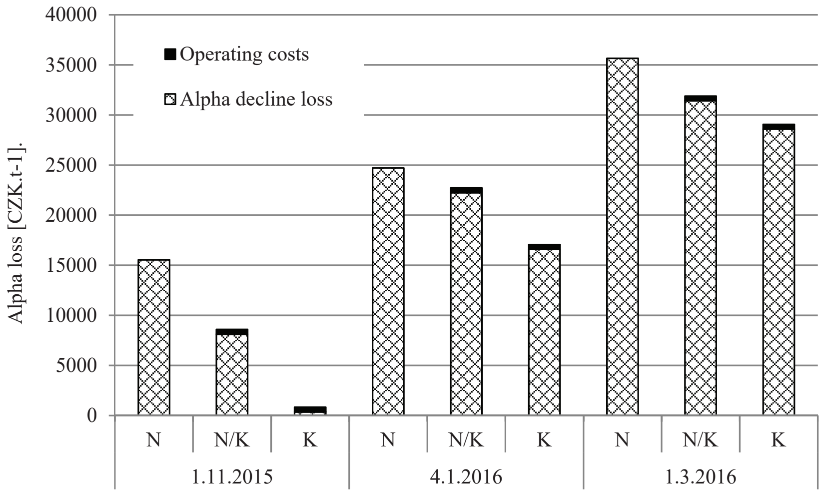
When comparing an air-conditioned and non-conditioned warehouse, increased operational costs need to be taken into account in case of a non-conditioned warehouse. Based on multi-annual records provided by the hop processor, an increase related to 1 t of dry hops stored in the air-conditioned warehouse results as follows:

Electricity consumption of the air-conditioner (to 5°C)	183.70 CZK t^{-1}
Depreciations (technical upgrading)	275.00 CZK t^{-1}
Annual service for refrigerating equipment	14.81 CZK t^{-1}
In total	473.51 CZK t^{-1}

CONCLUSION

The following conclusions can be drawn from the measurements performed: the graph in Fig. 3 clearly shows the financial losses related to the decline in the alpha content, rising significantly with hop storage duration before the final processing and they are also higher with a non-conditioned warehouse than with an air-conditioned one. The above mentioned operational costs are also included in the graphical presentation with the air-conditioned warehouse (Fig. 3, see the red marking). The lowest losses in alpha are recorded

Fig. 3. Losses caused by decline of alpha depending on storage time and place



in the case of up to two-month-long storage in the air-conditioned warehouse. When stored for a longer period, a more progressive increase in alpha losses occurs in the air-conditioned warehouse compared to the non-conditioned one, nevertheless storing in this warehouse is more advantageous.

The identified (Table 4) and illustrated (Fig. 3) values clearly indicate a significant profit in the price of alpha contained in 1 t of hops stored in the air-conditioned warehouse. At the date of 1/11/2015 this profit was 14 706 CZK, at the date of 4/1/2016 it was 7646 CZK, and at 1/3/2016 the profit was 6587 CZK. This calculation also includes the costs of operating the air-conditioned warehouse. The implemented measurements and the inferred results document the effectiveness of air-conditioned warehouses intended for baled hops before their further processing.

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