STORAGE STABILITY OF HYBRIDS – IMPORTANT HOP QUALITY TRAIT

Andreja ČERENAK[1], Iztok Jože KOŠIR[1]

UDC / UDK 633.791:631.52:631.563.8 (045)
original scientific paper / izvirni znanstveni članek
received / prispelo: 28.09.2009
accepted / sprejeto: 21.12.2009

ABSTRACT

Storage stability is a very important hop quality trait especially in the time of overproduction. As other important agronomic traits, storage stability is a characteristic observed in all perspective hop hybrids included in the Slovenian breeding programme. Based on the results obtained in the past few years, it can be concluded that hop germplasm at Slovenian Institute of Hop Research and Brewing has a great potential in terms of good storage stability.

Keywords: hop, *Humulus lupulus* L., storage stability, hybrid

SKLADIŠČNA OBSTOJNOST KRIŽANCEV – POMEMBNA LASTNOST KAKOVOSTI HMELJA

IZVLEČEK

Skladiščna obstojnost je zelo pomembna lastnost hmelja zlasti v obdobju viškov hmelja. Kot ostale agronomsko pomembne lastnosti je skladiščna obstojnost lastnost, ki se ocenjuje pri vseh perspektivnih križancih hmelja vključenih v slovenski žlahtniteljski program. Glede na rezultate zadnjih nekaj let se lahko zaključi, da ima dednina hmelja na Inštitutu za hmeljarstvo in pivovarstvo Slovenije dober potencial v smeri skladiščne obstojnosti.

Ključne besede: hmelj, *Humulus lupulus* L., skladiščna obstojnost, križanec

[1] Slovenian Institute of Hop Research and Brewing, Cesta Žalskega tabora 2, SI-3310 Žalec, Slovenia

1 INTRODUCTION

Hops have three main metabolites relevant to brewers: alpha-acids, beta-acids, and essential oils. Brewers normally concern themselves with only two of the three: alpha-acids and essential oils. Hops start to lose their alpha-acids and essential oils as soon as they are harvested. The rate of loss depends on the storage temperature, the amount of air (oxygen) present, and the hop variety, of which the most important factor we have control of is temperature, followed by a hop variety, and finally aerobic or anaerobic storage conditions.

The lower the temperature, the less of the hop metabolites deteriorate. It has been established that the rate of loss halves at every 15 °C drop in the temperature [3].

Oxygen is a non-pleasant parameter in hop storage; oxidized alpha-acids lose their bitterness and cannot be isomerised. They are responsible for the "cheesy" aroma detected in old hops. The compression of hops into bales, pellets, and plugs provides good protection against air exposure to all hop parts except the surface layers, and even then the air penetrates and causes oxidation. Exposure to light hastens hop deterioration as well [6,7].

A **hop variety** also plays a major role in storage. Hops are usually classified as kettle or bitter hops, and aroma hops. Kettle hops have a higher alpha-acid content than aroma hops, and their storage properties are more important. Under identical storage conditions, certain varieties will lose more alpha-acids than others.

As a result of oxidation and auto oxidation processes in hop cones in the time of storage, composition and the amount of hop resins, essential oils and polyphenols changes. The reasons for the difference in storage stability between different varieties are:

- The content of enzyme alpha-acid oxidase,
- The content of endogenous antioxidants,
- Membrane permeability of lupulin glands for oxygen [8].

Determination of storage stability is based on the decrease of alpha-acid content in the given time. For this purpose 2 parameters are used - the alpha-acid content and hop storage index (HSI). HSI parameter is a number obtained by spectrophotometric determinations of alpha-acids; it is a ratio between alpha-acid content and their oxidation products. Nickers and Menary [5] have proposed the following criteria for storage stability of hop varieties stored for 6 months at 20 °C:

- Very good storage stability: the varieties show 80-90 % of initial alpha-acid content
- Good storage stability: the varieties show 60-80 % of initial alpha-acid content
- Poor storage stability: the varieties show less than 50 % of initial alpha-acid content

There is a direct relationship between the losses of alpha-acid content and hop storage index (HSI). If the present alpha-acid content and HSI, or the percentage lost figures for a particular variety is known, the original and future alpha-acid content could be estimated. Hop quality during the storage is identical to the 'degree of freshness' – Table 1 shows the reduction of alpha-acid content and the HSI divided into 5 categories [2].

Table 1: Hop quality expressed as alpha-acid losses and HSI during the storage [2]
Preglednica 1: Kakovost hmelja izražena z izgubami alfa-kislin in HSI med skladiščenjem [2]

Classes of hop freshness	Deterioration of alpha-acids (% rel.)	Hop storage index
Fresh	0 – 10	< 0.32
Slightly aged	11 – 20	0.33 – 0.40
Aged	21 – 30	0.41 – 0.50
Strongly aged	31 – 40	0.51 – 0.60
Overaged	> 40	>0.61

Oils also reduce and oxidize over time. An assumption could be made that the rate of oil loss is directly related to the loss of alpha-acids therefore oil losses can be predicted with the use of alpha-acid loss formulas. Due to the lack of experimental data to support this method, it remains only an assumption [3].

Since storage stability as a parameter of each new variety is an important property, we have included monitoring of both indicators (loss of alpha-acids, HSI) in the breeding process. The aim of prolonged storage period (2 years) was to determine the storage stability of accessions in the time when using hops in breweries is still an option, especially in the time of overproduction of hops.

2 MATERIAL AND METHODS

2.1 Material

In this research perspective hop hybrids from Slovenian hop breeding programme and Dana bitter variety were included (Table 2). Hybrids 279/54, 279/104, 279/122 bred for their bitter acids and Dana were stored for 2 years at 20 °C and 4 °C. The research also included hops stored at 4 °C as nowadays the majority of hops are kept in cold storage. The absence of light was assured in both cases.

The trial started after harvest in 2006. In the last year 5 new perspective hop hybrids labelled as 31/299 (noble hop aroma, high resistance to verticilium wilt), A6/58 (dual purpose, high resistance to verticilium wilt), 285/70 (bitter type), 40/39 (bitter type), A2/132 (bitter type, high resistance to verticilium wilt) were added. The samples were included in the analyses for one year; the trial was carried out after harvest in 2008 (Table 4).

2.2 Methods

All samples were picked in the time of their technological maturity (end of August / beginning of September) on the experimental farm of Slovenian Institute of Hop Research and Brewing in Žalec. In order to obtain the initial values, first determinations of Lead Conductance Value (LCV) and HSI were carried out straight after the harvest. All other determinations were done in the intervals of approximately two months after the harvest time.

To determine LCV value in hop cones Analytica EBC, 7.4 [1] method was used. 50 mL of toluene (S ≤ 0,002 %) (Fluka) was added to the milled hop cones (5 g) and samples were then

shaken for 30 min. After filtration, 40 mL of methanol (ρ = 0,79 g/mL) (Fluka) was added to 10 mL of toluene extract, folowed by titration with the lead acetate solution (min 99,9 %) (Ridel de Haën) on the Conductometer MeThrom 712. The results were evaluated with software TiNet 2.4 (Herisau, Switzerland). Standardization of lead acetate solution before each series of measurements was carried out.

Hop storage index value was determined with ASBC method [4].

3 RESULTS AND DISCUSSION

3.1 Two-year trial

Dana variety

After a six-month storage period at 20 °C the alpha-acid content decreased for 4.3 % (rel.) and for 3.3 % (rel.) when hops were stored at 4 °C. HSI increased by 0.03 up to 0.37 at room temperature and at 4 °C (Table 2). Very good storage stability of the variety was recorded after 6 months.

In one year period alpha-acid content fell by 42.5 % (rel.) and by 27.5 % (rel.) at 20 or 4 °C. The results obtained have shown that Dana variety has good storage properties even after 2 years of storage. During a two-year storage period the alpha-acid content decreased by 60 % (rel.) and by 46.7 % (rel.) at 20 °C or 4 °C respectively (Table 2).

Hybrid 279/122

After a six-month storage period at 20 °C or 4 °C the alpha-acid content decreased for 5.8 % (rel.) and 2.9 % (rel.) respectively. It was observed that in the same time and in the same conditions HSI increased from 0.11 up to 0.50 at room temperature, or from 0.04 up to 0.43 at 4 °C.

It can be concluded that hybrid 279/122 has very good storage stability. After a two-year storage period at 20 °C the alpha-acid content decreased by 68.0 % (rel.) and at 4 °C by 47.6 % (rel.). In the same time the HSI increased to 1.80 and 0.73 at 20 °C or 4 °C respectively (Table 2).

Hybrid 279/104

After a six-month storage period at 20 °C the alpha-acid content decreased for 14.0 % (rel.) when hops were stored at 4 °C alpha-acids content fell by 0.1 % (rel.). HSI increased by 0.03 up to 0.29. All data show that hybrid 279/104 has very good storage stability. After a two-year storage period at 20 °C the alpha-acid content decreased by 46.3 % (rel.) and at 4 °C by 26.4 % (rel.). In the same time HSI increased to 0.53 at 4 °C (Table 2). The results obtained have shown that even after 2 years of storage hybrid 279/104 has very good storage properties.

Hybrid 279/54

After a six-month storage period at 20 °C the alpha-acid content decreased for 13.3 % and by 9.7 % (rel.) at 4 °C. When hops were stored at 20 °C HSI increased by 0.08 up to 0.48. After 6 months hybrid 279/54 has very good storage stability. After a two-year storage period at 20 °C the alpha-acid content decreased by 57.5 % (rel.) and at 4 °C by 44.2 % (rel.). In the same time HSI increased to 1.22 at 20 °C (Table 2).

In 2008 we repeated the trial with the above mentioned hybrids and Dana to confirm the results from the previous year since each production year has different climate characteristics (Table 3). It can be seen from Table 3 that the same results were obtained as in the previous year which means that all three hybrids including Dana variety were characterised as hops with very good storage stability.

3.2 New perspective hybrids

After a six-month storage period at 20 °C the alpha-acid content losses for 5.8 % to 18.0 % were recorded in hybrids **31/299, A6/58, 285/70, 40/39** and **A2/132** (Table 4). HSI increased in the same time in the same conditions by 0.02 up to 0.14, depending on the observed hybrid. After one-year storage period at 20 °C the alpha-acid content decreased from 21.2 % (rel.) to 49.1 % (rel.), and at 4 °C from 5.1 up to 20.9 % (rel.). In the same time the HSI increased from 0.03 up to 0.17 at 4 °C, or from 0.22 up to 0.64 at 20 °C (Table 4).

After a six-month storage period at 20º C all hybrids were classified as hops with very good storage stability.

Table 2: The alpha-acid content and HSI values in samples after a two-year storage period at 4 and 20 °C (harvest 2006)
Preglednica 2: Vsebnosti alfa-kislin in vrednost HSI v staranih vzorcih hmelja tekom dveh let pri temperaturah 4 °C in 20 °C (letnik 2006)

Hybrid			Initial	6 months	9 months	12 months	15 months	19 months	24 months	Storage stability
279D112 (Dana)	α-acids	4	12.0	11.jun	11.jun	8.jul	8.feb	7.maj	6.apr	Very good
		20		11.maj	9.avg	6.sep	6.apr	5.avg	4.avg	
	HSI	4	0.34	0.37	0.39	0.39	0.54	0.74	1.jun	
		20		0.37	0.53	0.64	0.83	0.99	jan.29	
279/122	α-acids	4	10.mar	10.0	10.0	7.sep	7.jul	7.0	5.apr	Very good
		20		9.jul	7.mar	5.avg	5.feb	4.jul	3.mar	
	HSI	4	0.39	0.43	0.43	0.45	0.48	0.56	0.73	
		20		0.50	0.81	0.82	jan.21	0.88	jan.80	
279/104	α-acids	4	12.jan	12.0	11.avg	11.sep	11.jul	10.jun	8.sep	Very good
		20		10.apr	10.apr	8.avg	7.jun	7.feb	6.maj	
	HSI	4	0.26	0.26	0.27	0.28	0.34	0.42	0.53	
		20		0.29	0.34	0.36	0.40	0.57	0.77	
279/54	α-acids	4	11.mar	10.feb	8.feb	7.feb	7.feb	6.avg	6.mar	Very good
		20		9.avg	7.maj	5.maj	5.mar	5.jan	4.avg	
	HSI	4	0.36	0.42	0.51	0.55	0.66	0.72	1.jan	
		20		0.48	0.59	0.65	0.83	0.98	jan.22	

Table 3: The alpha-acid content and HSI values in samples after one-year storage period at 4 and 20°C (harvest 2008)
Preglednica 3: Vsebnosti alfa-kislin in vrednosti HSI v staranih vzorcih hmelja pri temperaturah 4 in 20 °C tekom enega leta (letnik 2008)

Hybrid			initial	3 months	6 months	8 months	10 months	12 months	Storage stability
279D112 (Dana)	α-acids	4	16.sep	16.maj	16.0	15.avg	15.maj	15.apr	Very good
		20		16.feb	15.mar	13.apr	10.mar	9.0	
	HSI	4	0.29	0.29	0.30	0.34	0.38	0.39	
		20		0.35	0.40	0.53	0.71	0.88	
279/122	α-acids	4	15.mar	14.sep	14.maj	14.apr	14.apr	14.mar	Very good
		20		15.jan	14.0	13.sep	13.jun	11.apr	
	HSI	4	0.28	0.28	0.28	0.29	0.32	0.33	
		20		0.29	0.31	0.36	0.46	0.49	
279/104	α-acids	4	15.jan	13.0	13.mar	12.jul	12.jun	12.jun	Very good
		20		13.apr	12.apr	10.maj	9.sep	9.0	
	HSI	4	0.27	0.28	0.29	0.30	0.35	0.37	
		20		0.30	0.32	0.40	0.50	0.56	
279/54	α-acids	4	13.mar	12.avg	12.jul	12.maj	12.maj	12.jan	Very good
		20		12.maj	11.jul	10.maj	7.avg	8.maj	
	HSI	4	0.26	0.27	0.30	0.33	0.39	0.39	
		20		0.32	0.37	0.50	0.67	0.78	

Table 4: The alpha-acid contents and HSI values in hybrids 31/299, A6/58, 285/70, 40/39 and A2/132 after one-year storage period at 4 and 20°C (harvest 2008)
Preglednica 4: Vsebnosti alfa-kislin in vrednost HSI v staranih vzorcih hmelja pri temperaturah 4 in 20 °C križancev 31/299, A6/58, 285/70, 40/39 in A2/132 (letnik 2008)

hybrid			initial	3 months	6 months	8 months	10 months	12 months
31/299	α-acids	4	5.apr	4.jun	4.jun	4.maj	4.apr	4.apr
		20		4.jun	4.maj	4.jan	3.mar	3.feb
	HSI	4	0.28	0.28	0.32	0.33	0.41	0.43
		20		0.37	0.39	0.48	0.66	0.67
A6/58	α-acids	4	10.maj	11.feb	10.feb	9.0	9.mar	8.mar
		20		10.jun	9.mar	9.feb	6.0	5.apr
	HSI	4	0.28	0.29	0.32	0.35	0.42	0.44
		20		0.35	0.42	0.53	0.71	0.88
285/70	α-acids	4	16.jul	16.jun	16.mar	15.sep	15.feb	14.jul
		20		12.sep	12.jul	11.mar	9.jul	8.maj
	HSI	4	0.27	0.27	0.28	0.30	0.34	0.34
		20		0.35	0.39	0.52	0.62	0.68
40/39	α-acids	4	13.jul	13.jul	13.mar	13.0	12.avg	12.feb
		20		12.apr	12.0	11.sep	10.sep	10.avg
	HSI	4	0.25	0.26	0.28	0.28	0.29	0.29
		20		0.29	0.29	0.30	0.38	0.89
A2/132	α-acids	4	15.jan	14.sep	14.avg	14.maj	14.mar	14.0
		20		15.jan	13.sep	13.sep	13.jun	11.apr
	HSI	4	0.27	0.28	0.28	0.29	0.32	0.33
		20		0.29	0.31	0.36	0.46	0.49

4 CONCLUSIONS

It can be concluded that hybrid 279/104 has excellent characteristics after two years of storage; its HSI was 0.77 or 0.53 stored at room or cold temperature respectively. Very good storage stability was also observed in Dana variety. Hybrids 279/54 and 279/122 showed slightly worse results but they were still classified as the ones with good storage properties.

New perspective hybrids 31/299, 285/70, 40/39, A6/58 and A2/132 still show very good storage stability after 1 year of storage in cold conditions.

In the time of overproduction of hops on the global hop market the development of own varieties with very good storage stability is becoming even more important. Storage stability is an important hop trait and an indicator of stability of the main hop metabolites during storage therefore it is essential for maintaining hop quality in the whole hop industry (growers, merchants, brewers).

5 LITERATURE

1. Analytica-EBC/European Brewery Convention. Section 7 *Hops*, Method 7.4. Carl, Getränke Fachverlag (2000).
2. Foster, A., The quality chain from hops to hop products.- Proceedings of the Technical Commission IHGC of the 48th IHGC Congress, Canterbury (2001).
3. Garetz, M., How to get and keep your hops optimum value.- Brewing techniques, January/February (1994).
4. Methods of Analysis of the American Society of Brewing Chemists, 8th Edition, ASBC St. Paul, Minnesota, USA.
5. Nickers, G.B., Menary, R.C., Chemical evaluation of Hop Quality.- Annual Report, Oregon State University, Agriculture Chemical Department, Corvallis (1980).
6. Srečec, S., Rezič, T., Šantek, B., Marič, V., Hop Pellets Type 90: Influence of manufacture and Storage on losses of Alpha-Acids. - Acta Alimentaria, 38(2009)2, p. 141-147.
7. Virant, M., Majer, D., Hop storage index – indicator of a brewing quality.- Proceedings of the Technical Commission IHGC of the 49th IHGC Congress, Sofia (2003).
8. Zupanec, J, The effect of process parameters during optimisation of drying and supercritical extraction on quality of hop extract.- Doctoral thesis, University in Maribor, Technical Faculty Maribor (1992).