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Effect of drying temperature on the content and composition of hop oils

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ABSTRACT

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In terms of content, the paper is aimed at analysing and comparing the quality of fresh green hops and hops dried at two drying temperatures – 55°C (in the traditional manner) and 40°C (using the so-called gentle drying), regarding the maximum preservation of hop essential oils. Comparative experiments were carried out in an experimental chamber dryer with two Czech hop cultivars Saaz and Harmonie. The moisture content of hops at the beginning of drying was 75% and at the end of drying it was 9–10%. By lowering the drying temperature from 55°C to 40°C, the drying time in cv. Saaz prolonged from 8 to 10 h and for the cv. Harmonie from 9 h to 12 h. Compared to fresh hops, the amount of hop oils decreased by 10% when dried at 40°C and by 36% (cv. Saaz) and 43% (cv. Harmonie) when dried at 55°C. These losses can be considered significant, especially for hops intended for late and dry beer hopping. However, by drying the hops at different temperatures, the ratios between various components of the essential oils and thus also their sensory character remained approximately unchanged. Due to the reduced amount of essential oils, the drying effect reduces the intensity of hop aroma depending on the drying temperature.

Keywords: hop cones; *Humulus lupulus* L.; terpenic hydrocarbons; beer industry; distillation method

Hop essential oils are the most important group of technologically important hop substances responsible for the characteristic hops aroma. They are a mixture of several hundred natural volatile substances of different chemical composition. Some are represented in the order of tens of percent (means relative to the total content of essential oils), others occur in small to trace amounts. The largest portion belongs to terpenic hydrocarbons like myrcene, β-caryophyllene, α-humulene, β-farnesene and selinenes, which make up 60–80% of the total weight of essential oils. The remaining part is the oxygen fraction, which is much richer in composition, because it contains a wide range of esters, ketones, aldehydes, alcohols and epoxides. A small percentage (about 1%) is formed by sulfur substances. Conventional drying at a temperature of 55–60°C results in irreversible transformations and losses of essential oils that reduce the product quality. Pilot studies have shown that under the current drying temperatures of 55–60°C, the total amount of essential oils is reduced by 15% to 25% compared to conditions before drying (Henderson 1973). During wort boiling, a major part of essential oils evaporates from the brew kettle with water steam. In order to achieve more intense hop aroma in beer, the hops are added in several batches, with the last addition being dispensed just

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before the end of the boiling. Another technological option for enhancing the hops flavour in beer is the addition of hops during post-fermentation as so-called 'dry hopping'. During dry hopping, some hop oils components that evaporate from the kettle during wort boiling without utilisation, enrich sensorial profile of beer. Ethanol also contributes to the release of hop oils components into beer. This process is particularly widespread in the segment of small craft breweries producing beers such as India Pale Ale, Imperial IPA, New England IPA and other beer brands, but is often used in the production of lagers or alcohol-free beers in large industrial breweries. The number of small breweries in the Czech Republic is currently around 400 and construction of more is planned.

High doses of hops ranking mostly from 100 to 500 g/hL are typical for technology of dry hopping (Mitter and Cocuzza 2013). The amount of hops is often determined based on the content of the essential oils, or on the basis of the content of selected compounds (linalool) (Forster and Gahr 2013). For dry hopping, it is therefore the most desirable to keep the amount and composition of hop essential oils in their original state before drying. One way to achieve this is the concept of so-called low temperature drying at the maximum drying air temperature of 40°C (Hofmann et al. 2013).

The presented study summarizes the results of determining both the content and composition of hop essential oils during drying two Czech hop cultivars at low temperature in an experimental chamber dryer which was designed and produced for this purpose. The results are compared with the data obtained when the hops were dried at 55°C, and fresh hops which were not subjected to any heat load.

MATERIAL AND METHODS

Hops drying was carried out at temperatures of 55°C and 40°C during hop harvest, which lasts about one month from mid-August to mid-September. For the purposes of drying at both temperatures, an experimental chamber dryer with dimensions of 900 × 900 × 300 mm and a capacity of 20–23 kg of fresh hops was manufactured (Figure 1). The kiln is heated up by an electric hot air unit of 18 kW power consumption. The heated air is sucked into the dryer by the RSH 500 fan and using flaps it is directed to the entire floor area of the drying chamber. Above the hops layer there is an APZC630 exhaust ventilator with a capacity of 1.5 kW for forced outflow of air passing through the layer of hops (Heřmánek et al. 2017, Rybka et al. 2018).

Sensors for measuring temperature and relative humidity of drying air as well as its pressure and velocity were placed below and above the hop layer. Three dataloggers were inserted into the hop layer to continuously measure the temperature and relative humidity. During the drying, hops samples were taken to determine the moisture content (Rybáček et al. 1980, Kumhála et al. 2016).

During the harvest, just prior to drying, fresh green hops were collected in the amount of about 25 kg. This allowed regular and low temperature drying tests to be carried out, and at the same time to perform analyses of the content and composition of hop oils in fresh green hops that had not been exposed to any heat load. Analytical values for fresh hops served as referential for assessing the effect of drying temperature on quality. Samples of hops dried at 55°C and 40°C were collected at the target moisture of a regular drying cycle (9–10%). Drying tests were carried out with two Czech cultivars of hops, Saaz and Harmonie. Both cultivars contain different amounts of essential oils and differ also in their composition. A high content of -farnesene (about 20%) is typical for cv. Saaz, cv. Harmonie contains a significant amount of α- and β-selinenes (10% to 15%).

A steam distillation method at atmospheric pressure was used to isolate hop oils from the hop ma-

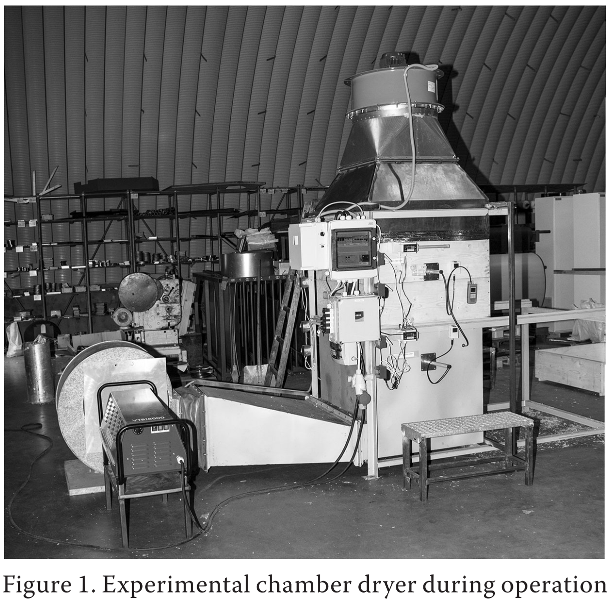

Figure 1. Experimental chamber dryer during operation

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trices (Kralj et al. 1991). Ground hops (100 g) were added to 4000 mL of water and the mixture was boiled for 90 min. Fresh hop cones (150 g) were cut into smaller pieces before the oils separation. The hop oils content was recalculated to an absolutely dry matrix on the basis of moisture content. The composition of the hop oils was determined by gas chromatography on gas chromatograph focus coupled with a DSQ II mass detector (Thermo Fisher Scientific, San Jose, USA). Analyses were performed using a capillary column DB5, 30 m × 0.25 mm × 0.50 µm (Agilent). Column temperature was programmed in the interval of 60°C to 250°C. Helium carrier gas was supplied at a head pressure of 60 kPa to provide the initial flow rate of 1.5 mL/min. Samples of the hop oils were diluted in n-hexane in a 1:1 ratio and injected on analytical column at a rate of 0.5 µL in a 25:1 split ratio. The mass spectra were obtained in electron impact ionization mode at 70 eV. Identification of the substances was performed using the NIST (National Institute of Standards and Technology) mass spectra library and comparing the retention times of authentic standards. With the help of Xcalibur software 12 (Waltham, USA), essential components of terpene and oxygen fraction were quantified in the essential oils.

All analyses were performed in three replicates. Statistical evaluation was carried out using the QC Expert program (TriloByte Statistical Software, Pardubice, Czech Republic). The data in the tables are expressed as medians of the primary analytical data.

RESULTS AND DISCUSSION

Effect of drying temperature on the content of essential oils. Figure 2 show the content of hop essential oils in green hops and hops dried at different temperatures of the drying air for the cultivars Saaz and Harmonie. The initial moisture content of the fresh hops in the mature state is 75 ± 2%, independent of the cultivar. The target moisture content of the hops at the end of drying was 9% to 10% in both cases. This is in order to avoid loosening of the cones, which occurs already with the moisture of the hops of about 5% to 6% and which would negatively affect the further processing of hops by, for example, granulation. The effect of an increased drying temperature on the amount of hop oils in dried hops is obvious. The amount of hop oils in the Saaz aroma cultivar declines in the order of green hops (1.09 g/100 g) – drying at 40°C (0.99 g/100 g) – drying at 55°C (0.70 g/100 g). For cv. Harmonie, the respective values are 2.38 g/100 g (green hops), 2.12 g/100 g (drying at 40°C) and 1.36 g/100 g (drying at 55°C). In relative terms, the loss of essential oils at a drying temperature of 55°C is 36% for cv. Saaz and 43% for the cv. Harmonie, if the value in the fresh green hops is taken as the reference. During drying at 40°C, the loss of essential oils is considerably lower and is only about 10%. Narziss and Forster (1972) came to a similar conclusion, pointing to losses of 10% to 60% depending on drying conditions and hop cultivar. Münsterer and Kammhuber (2015) carried out hop drying at temperatures of 60, 65 and 70°C and did not detect any significant effect of drying temperatures on either the amount or the composition of hop oils, which – as far as the amount of essential oils is concerned – partly contradicts our data. As a comparative measurement, however, they used the method of cryogenic drying (lyophilization), which is performed at low temperatures and high vacuum. Different results can be caused by the diverse drying temperatures.

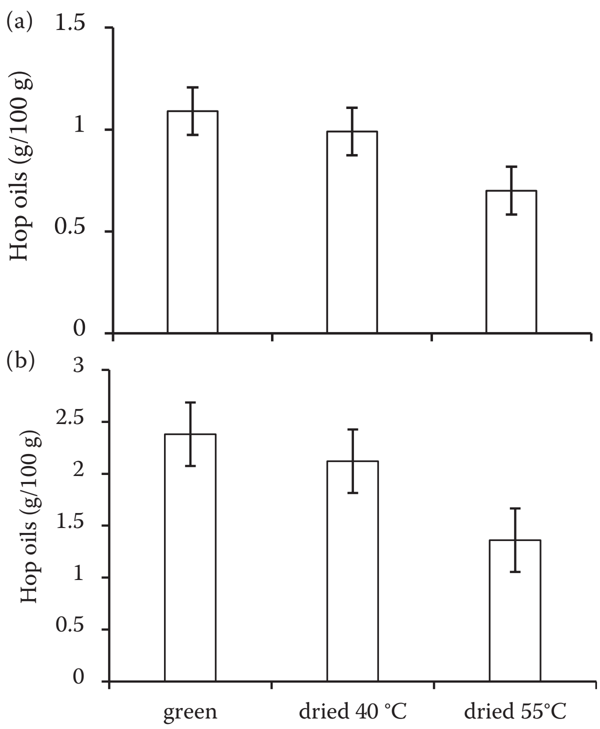

Figure 2. The content of essential oils in green hops and hops dried at different temperatures of drying air – (a) cv. Saaz and (b) cv. Harmonie

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Table 1. Composition of hop oils in cvs. Saaz and Harmonie in fresh and dry cones dried at different temperatures. The figures are given in % and express the relative content of the component in the total amount of essential oils

Component	Cv. Saaz			Cv. Harmonie		
	green	40°C	55°C	green	40°C	55°C
β-Pinene	0.52	0.57	0.55	0.95	0.87	0.95
Myrcene	23.00	24.00	24.00	37.20	35.70	33.10
Limonene	0.13	0.13	0.11	0.22	0.19	0.20
Linalool	0.45	0.45	0.35	0.93	0.70	0.77
Geraniol	0.31	0.15	0.17	0.28	0.13	0.21
2-Undecanone	1.38	1.26	1.10	0.69	0.57	0.69
α-Caryophyllene	8.30	8.40	8.20	7.70	8.40	8.80
β-Farnesene	21.30	21.60	21.20	0.11	0.09	0.19
β-Humulene	23.10	24.80	24.60	21.10	22.40	22.10
Selinenes	1.06	1.12	1.09	12.90	15.30	14.80
Caryophyllene epoxide	0.23	0.22	0.34	0.13	0.09	0.14
Humulene epoxide II	0.50	0.41	0.70	0.19	0.13	0.25

Effect of drying temperature on the composition of essential oils. Table 1 summarizes the data characterizing the composition of hops in fresh green hop cones and hops dried at 40°C and 55°C. The major terpenic hydrocarbons (myrcene, α-caryophyllene, β-humulene, β-farnesene and selinenes) together with several important representatives of the oxygen fraction (linalool, geraniol, 2-undecanone) account for 70% to 80% of the total content of essential oils. The statistical assessment of the significance of differences in composition of individual hop oils was done by the paired *t*-test. The results showed that differences in the composition of hop oils within one cultivar are not statistically significant in either of the pairs considered, i.e. green – 40°C, green – 55°C, 40–55°C. Analytical data show that during drying the components of the hop oils volatilize at about the same extent. By drying the hops, the ratio between the components of the essential oils and thus also their sensory profile and character is maintained.

However, due to the reduced amount of essential oils, the drying of hops reduces intensity of its aroma depending on the drying temperature. On the contrary, as expected, statistically significant

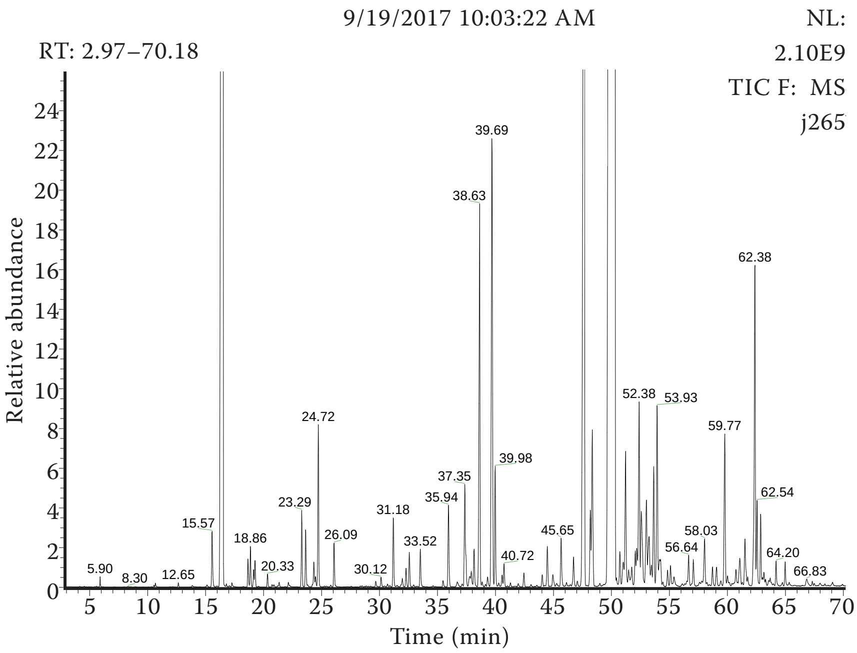

Figure 3. A typical chromatogram of hop oils of the Saaz cultivar isolated from fresh green cones (GC/MS, DB5-MS, 30 m × 0.25 mm × 0.50 μm, temperature programme 60–250°C, characteristic compound β-farnesene, retention time 49:75 min)

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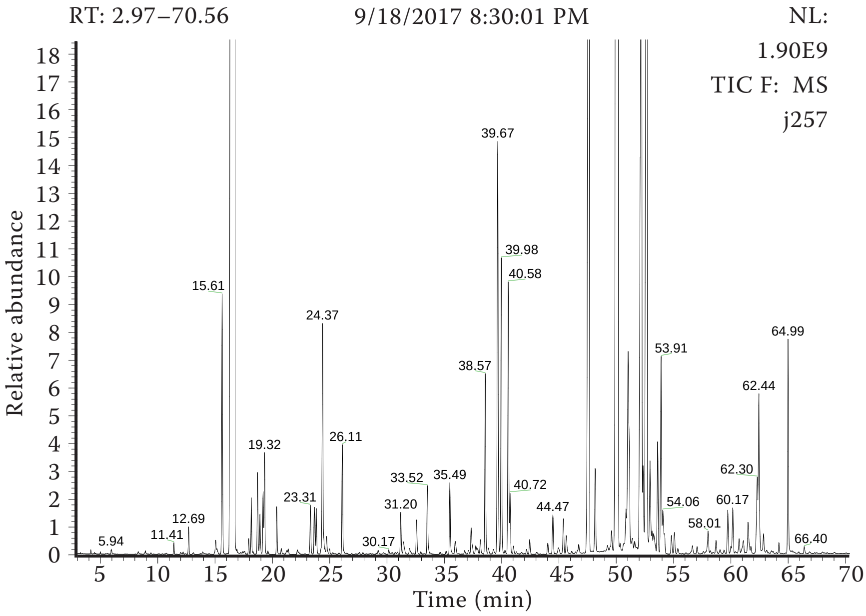

Figure 4. A typical chromatogram of hop oils of the Harmonie cultivar isolated from fresh green cones (GC/MS, DB5-MS, 30 m × 0.25 mm × 0.50 µm, temperature programme 60–250°C, characteristic compound β-selinene, α-selinene, retention times 52:10 min and 52:56 min)

difference in composition of the hop oils between the Saaz and Harmonie cultivars was confirmed, mainly due to differences in β-farnesene and selinenes content (Figures 3 and 4). However, the composition of hop oils is significantly influenced by the degree of maturity of the hop cones and the term of harvest (Vitázek and Havelka 2014, Münsterer 2017). Both factors are determined by the course of weather conditions during the growing season.

Low-temperature drying of hops is a promising way of gentle preservation of hops, which retains 90% of the original content of flavouring substances at a comparable composition, compared to fresh hops. The lower drying temperature is compensated by longer drying time, so the energy demand of the low temperature (40°C) and standard (55°C) hop drying is comparable. Lower equipment capacity and possibly higher wage costs are offset by higher utility value of hops. Low temperature drying technology is especially suitable for some special hop cultivars (flavour hops) that are intended for dry hopping or for those cultivars with a high content of thermolabile, health-promoting substances.

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