10TH TRENDS IN BREWING
Ghent, Belgium. April 1st-5th 2012

Fingerprinting of hop oil constituents and sensory evaluation of the essential oil of hop pellets from pure hop varieties and single-hop beers derived thereof

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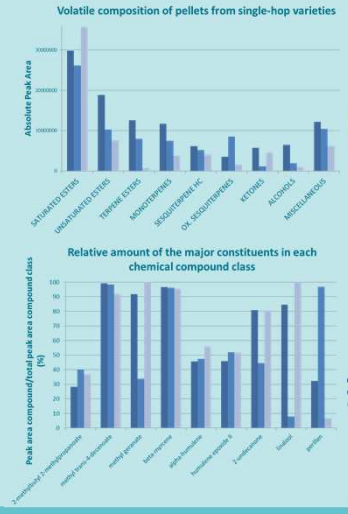
INTRODUCTION

Hops impart both bitterness and hoppy aroma to beer. In respect of hoppy aroma, late- and dry-hopping techniques are applied to prepare beers with a pronounced, varietal dependent hop aromatic character. The characteristic hoppy odour/aroma of the final beer prepared via late- and dry-hopping is mainly determined by the hop variety used and is caused by the volatiles originally present in, or derived from, hop essential oil. In this study, we aimed at analytical and sensory characterisation of pellets from three distinctly different commercial hop varieties and six single-hop beers aromatised with these particular varieties. For each hop variety, two beers, i.e. late-hopped beer with and without an additional dry-hopping step, were brewed on a 40 hL scale. The presented results are part of a research project of which the main objectives are (1) to find sensory and analytical correlations between hops as raw material and the beers derived thereof, (2) accurate analytical measurement of hoppy aroma of beer, (3) determination of flavour-impact compounds for hop aroma and hoppy aroma of beer, and (4) study of the stability of hoppy aroma.

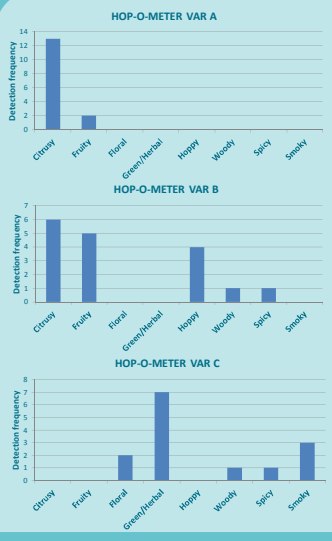
ANALYTICAL AND SENSORY ASSESSMENT OF HOP AROMA

ANALYTICAL FINGERPRINTING



- The volatile composition of pellets from three single-hop varieties (VAR A, VAR B, VAR C) was investigated via headspace solid-phase microextraction **(HS-SPME)** and gas chromatography-mass spectrometry **(GC-MS)**.
- More than 100 volatiles were detected and classified into several chemical compound classes.
- The **hop varieties** are clearly **differentiated** based on the **composition and level of each chemical compound class.**
- The relative amount of the most abundant volatile in each chemical compound class is graphically displayed showing **clear differences in composition of saturated esters, terpene esters, ketones, and alcohols** between the hop varieties investigated.

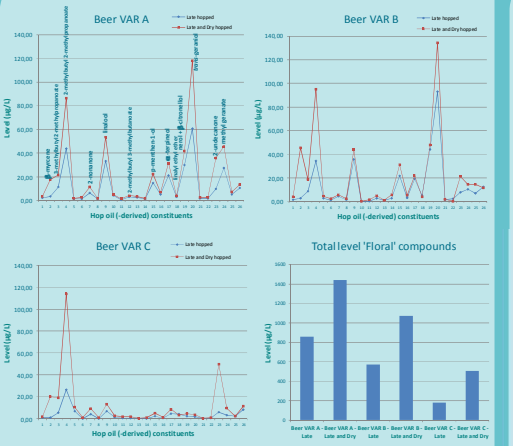
SENSORY PROFILES



- For sensory evaluations of hop aroma, the total essential oils of three hop varieties (VAR A, VAR B, VAR C) were selectively isolated from the hop pellets by supercritical fluid extraction using carbon dioxide.
- By adding appropriate amounts of the total essential oils to model solutions (ethanol-water, 5% v/v), the sensory properties were investigated and, as a result, **characteristic 'hop-o-meters'** reflecting the typical odour/aroma of each hop variety were established.
- Striking differences between the varietal hop oils were observed in respect of the descriptors 'Citrus' (grapefruit) - VAR A; 'Fruity/Citrus (orange)' and 'Hoppy' - VAR B; 'Green/Herbal' and 'Smoky' - VAR C.

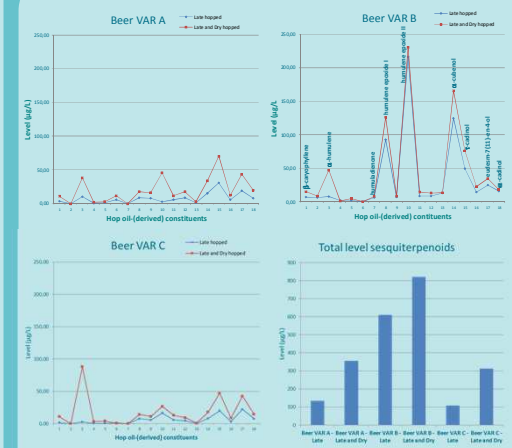
ANALYTICAL AND SENSORY ASSESSMENT OF HOPPY AROMA OF LATE- AND DRY-HOPPED BEERS

'FLORAL'-COMPOUND FINGERPRINTS



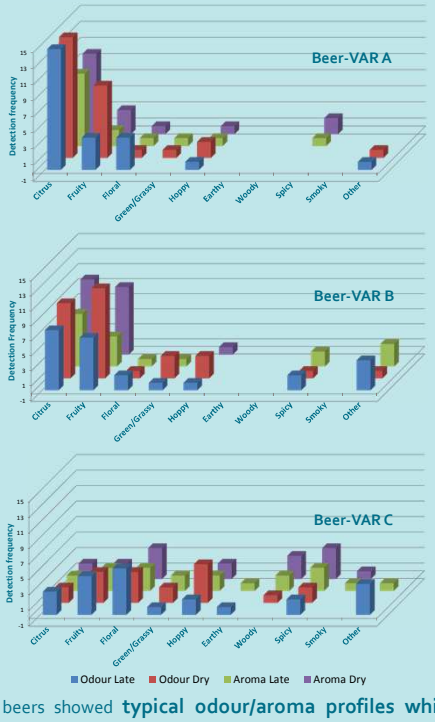
- The volatile composition of the beers, late- and dry-hopped with VAR A, VAR B or VAR C was determined via HS-SPME and GC-MS. **Extracted ion chromatograms** (m/z=58, 69, 71, 72, 74, 93, 136) were generated to detect hop oil (-derived) **monoterpenes and oxygenated compounds** ('Floral'-compounds).
- Based on the detection of 26 hop oil constituents originally present in hop essential oil (e.g. β-myrcene, linalool, geraniol, 2-undecanone, methyl geranate) and hop oil-derived constituents (e.g. α-terpineol, terpinyl ethyl ether) **characteristic analytical fingerprints** are obtained for each of the single-hopped beers investigated.
- Next to varietal differences between the beers, **differences between late- and dry-hopped beers brewed with the same variety** are observed.
- Dry-hopping increases the total level of floral compounds (1.7 (VAR A) – 2.8 (VAR C) times).

SESQUITERPENOID FINGERPRINTS



- The volatile composition of late- and dry-hopped beers was determined via HS-SPME and GC-MS. **Extracted ion chromatograms** (m/z= 69, 93, 109, 138, 161, 189, 204, 220, 222) were generated to detect hop oil-(derived) **sesquiterpenoids**.
- Based on the the detection of 18 hop oil constituents originally present in hop essential oil (e.g. β-caryophyllene, α-humulene, humulene epoxides) and hop oil-derived constituents (e.g. caryophyllenyl alcohol, humulol) **characteristic analytical fingerprints** are obtained for each of the single hopped beers investigated.
- The beers brewed with VAR B contained significantly higher levels of humulene epoxides. Higher levels of the oxygenated sesquiterpenes differentiated pellets of hop variety B from the other varieties.
- Dry-hopping increases the sesquiterpenoid level of the beers.

SENSORY PROFILES



All beers showed **typical odour/aroma profiles which reflect the sensory characteristics of the hop essential oils**. Beers hopped with VAR A or VAR B have pleasant and pronounced citrus (grapefruit) or citrus (orange)/fruity scents, respectively. The hoppy aromatic character of beers brewed with VAR C was less pronounced in terms of 'citrus' or fruity and was described using many descriptors (floral, hoppy, spicy, green/herbal, woody).

CONCLUSION

Characteristic analytical and sensory fingerprints of hop pellets from three distinctly different commercial hop varieties were obtained via HS SPME GC-MS and 'hop-o-meters' resulting from sensory evaluations of hop essential oil in model solutions. Analytical fingerprints of hop oil-derived constituents in the fresh beers show (1) significant differences between late- and dry-hopped beers brewed with the same hop variety, and (2) varietal differences between both late- and dry-hopped beers. The sensory properties of the varietal hop oils are clearly reflected in the resulting single-hop beers and, although further investigation is required, the presented data also point to a relationship between the analytical hop oil-derived profiles in the beers and the sensory perceptions of varietal hoppy aroma.

Acknowledgement: we would like to thank IWT Vlaanderen for financial support

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ANALYTICAL AND SENSORY ASSESSMENT OF THE FLAVOUR STABILITY IMPACT OF DRY-HOPPING IN SINGLE-HOP BEERS

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INTRODUCTION

Dry-hopping is a technique which is increasingly being applied in the production of specialty beers in order to impart additional and plant-original hoppy aroma notes. However, its impact on the flavour stability of beers is currently not well understood, especially regarding the specific contribution of the hop variety used. In this study, the flavour stability of a series of six single-hop beers derived from three distinctly different commercial hop varieties (A, B, C) was investigated.

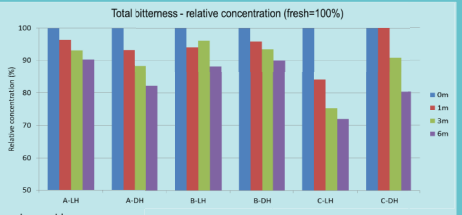
METHODOLOGY

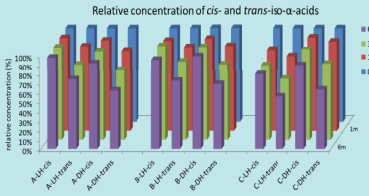
All beers were brewed and bottled on a semi-industrial scale (40 hl), and each beer was considered both before (late-hopped - LH) and after an additional dry-hopping step (dry-hopped - DH). The beers were immediately stored at 0°C to preserve freshness. For the evaluation of flavour stability, samples were aged in the dark at 25°C for 1, 3 and 6 months. Semi-quantitative determinations of hop oil-derived constituents were performed using HS-SPME in combination with GC-quadrupole MS operating in the selected ion-monitoring mode. Staling aldehydes in all beers were quantitatively determined using HS-SPME in combination with on-fibre PFBOA derivatisation and GC-MS. Quantitative determinations of the beer bitter acids were carried out through direct injection of the beer samples (in-house UPLC procedure). Sensory evaluation of flavour deterioration was performed by a trained panel (8 panellists), who were asked to give overall-ageing-scores (OAS: 0=not aged; 2=very lightly aged; 4=lightly aged; 6=clearly aged; 8=strongly aged/undrinkable) as well as to indicate a personal preference between the late- and the dry-hopped beer samples aged for 6 months.

ISO-α-ACIDS

- During ageing, a decline in total bitterness was observed for all the beers.

- As expected, *cis*-iso-α-acids were more stable than *trans*-iso-α-acids in all beers.

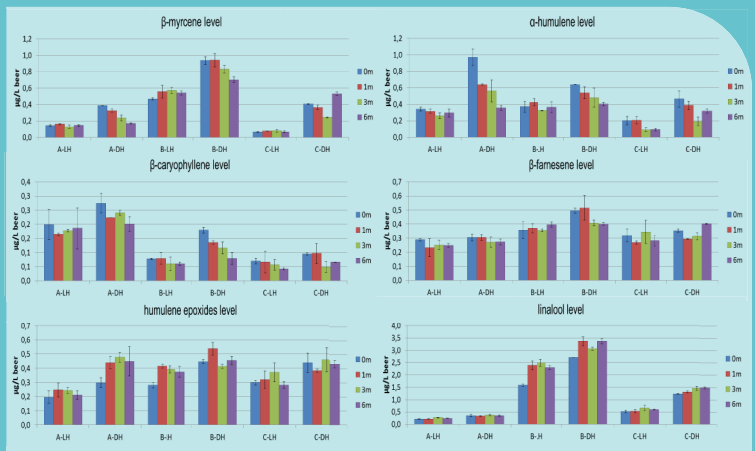




The decline in total bitterness was different **depending on LH versus DH**, but also depending **on the applied hop variety**:

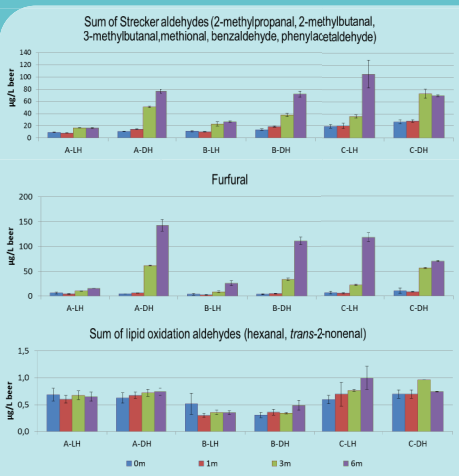
A: LH > DH
B: LH ≈ DH
C: LH < DH

HOP OIL-DERIVED CONSTITUENTS



β-myrcene concentrations in the dry-hopped beers were significantly higher than in the late-hopped beers and tended to **decrease with ageing**, whereas they remained fairly constant in the late-hopped beers. Similar behaviour could be observed for **α-humulene and β-caryophyllene**, while β-farnesene remained fairly constant during ageing regardless of the hopping regime. The sum of humulene epoxides I, II and III was found to be slightly higher in the dry-hopped beers, and did not change significantly during ageing. The amount of **linalool** in all beers appeared to **increase with ageing**, which has been attributed to the liberation of glycosidically bound linalool, according to the literature . After liberation from hop glycosides, linalool may contribute to the hoppy aroma of beer.

STALING ALDEHYDES



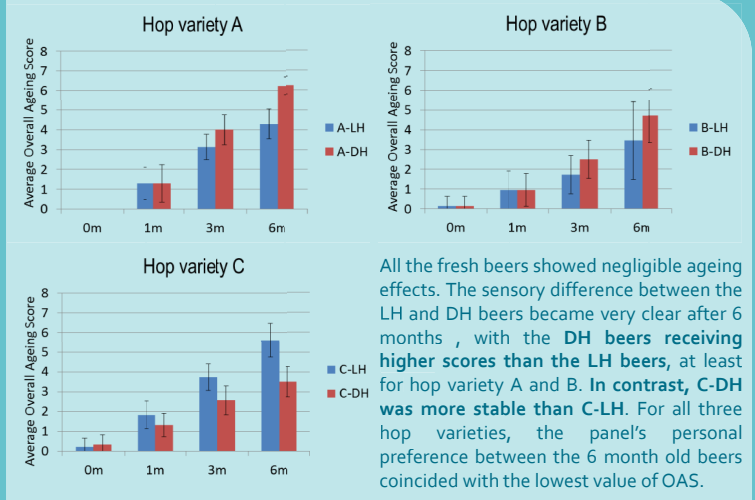
Aldehydes were observed to **increase with ageing time**.

After 6 months, **Strecker aldehydes** and **furfural** levels were **much higher for the DH beers**, with the exception of hop variety C.

Beer **C-LH** showed a significantly **higher increase than beer C-DH**.

The lipid oxidation aldehydes on the other hand, did not exhibit this trend, although C-LH did show a modest increase.

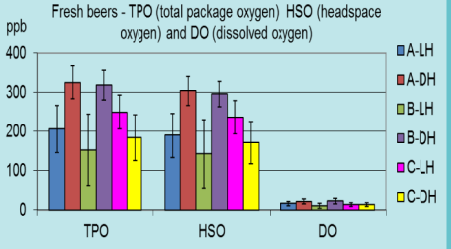
SENSORY EVALUATION



All the fresh beers showed negligible ageing effects. The sensory difference between the LH and DH beers became very clear after 6 months , with the **DH beers receiving higher scores than the LH beers**, at least for hop variety A and B. **In contrast, C-DH was more stable than C-LH**. For all three hop varieties, the panel's personal preference between the 6 month old beers coincided with the lowest value of OAS.

OXYGEN

DO and HSO were found to be lower in the LH beers for varieties A and B. For variety C, DO was comparable between the LH and DH beers, but HSO showed the lowest values for the dry-hopped beer. This may explain the difference in bitterness stability observed for hop variety C.



CONCLUSION

The above data suggest that the impact of an additional dry-hopping step on single-hop beer flavour stability is cultivar-dependent. The interplay of the degradation of iso-α-acids and hop oil-derived constituents on the one hand and the formation of staling aldehydes on the other hand is obviously a very intricate issue. However, the sensory results clearly reflect the analytical data. Whether oxygen content plays a significant role in the observed analytical and sensory changes upon ageing is unclear, but in any case, the dry-hopped beer C shows a markedly enhanced sensorial flavour stability compared to the other dry-hopped beers. Further research is needed in order to confirm these observations and to elucidate the possible underlying (bio-)chemical reasons for these interesting findings.

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