Influence of alcohol content on dry hopping

PILOT-SCALE STUDY | Dry hopping is applied to produce many different beer styles with varying alcohol contents. Information about the alcohol-dependent behaviour of hop components after dosing is necessary to understand interactions and to ensure consistent beer quality. A pilot-scale study was therefore performed using standardised procedures by only varying the beer's alcohol contents from 0.5 % to 10.5 % alcohol by volume (ABV) at constant dry hopping rate.

THE MAIN GOAL of dry hopping is to flavour beer by transferring hop volatiles on the cold side of beer production. For certain beer styles, dry hopping is a characteristic and essential part of the recipe but is also found to be highly suitable for beers with no or (very) low alcohol content. Non-alcoholic beers (NAB) in particular can lack in body and/or aroma and, depending on the dealcoholisation technique used, may also possess an unwelcome residual sweetness [1, 2].

In this case, dry hopping is one option to improve the overall flavour of a NAB. Changing the focus to beers with high(er) ABVs, dry-hopped beer types such as Belgian Style Triple or Double IPA (partly with 10.0% ABV and above) have been established on the market for many years. They indicate a boundary of the alcohol range of beer, not only as speciality beers [3].

Hence, dry hopping is a technique used for many beer categories with varying ABVs. The resulting interactions between hop components and ABVs have an influence on both, the sensory perception and also the beer's composition [4, 5]. This study investigated ABV-dependent behaviour of major volatile and non-volatile hop derived components, their transfer rates and corresponding side effects on beer attributes after dry hopping beer at different ABV. The details of the not hop-related effects are published in the corresponding paper of BrewingScience [6].

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Experimental set-up

A commercially available alcohol-free wheat beer (dealcoholisation via thermal evaporation) was used as a base beer to adjust the alcohol concentrations while keeping the hop dosing rate consistent at 250 g/hl using Type 90 Pellets of the variety Solero. The pellets were added loosely into 20 litre NC kegs. After a semi-static contact time of 14 days at a consistent temperature of 5 °C hop-derived bitter and aroma compounds were analysed according the latest MEBAK and/or EBC methods [7,8]. All analyses were carried out at the accredited central lab of Research Center Weihenstephan for Brewing and Food Quality, TU Munich, Freising, and the central lab of Hallertauer Hopfenveredelungsgesellschaft m.b.H., Mainburg, Germany.

The new aroma variety Solero was released in 2019 and is known for its fruity and tropical flavour [9], mainly attributed to hop esters, particularly isobutyl isobutyrate. Containing about 10 % total bittering substances, Solero represents a midrange composition of bitter acids. Table 1 provides an overview of the hop pellets utilised in this study.

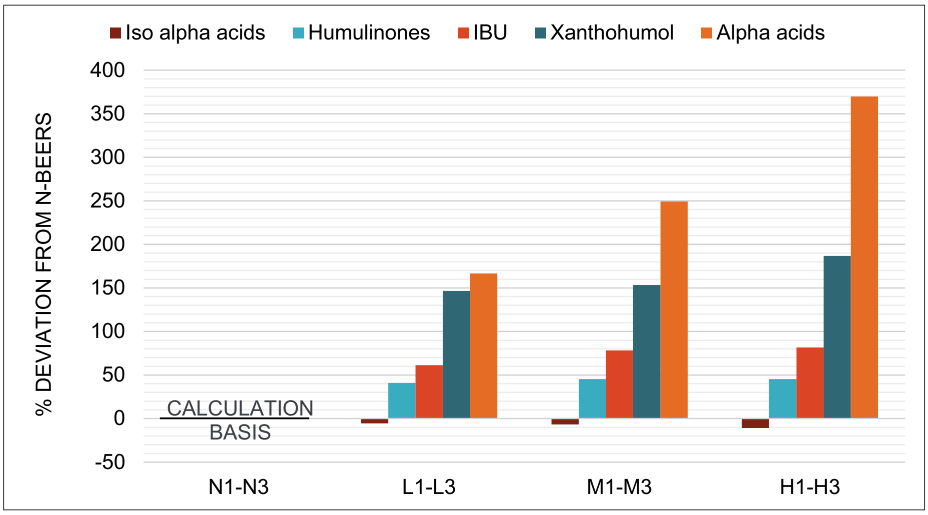

Fig. 1 Variations due to dry hopping of ethanol adjusted beers

Based on the base beer analyses, the quantity of purified ethanol to be added was calculated to reach an ABV of 0.5 %, 3.5 %, 7.0 % and 10.5 %. According to the ABV set in this way, the samples are designated as "N" (no), "L" (low), "M" (mid) and "H" (high) in the following. In this study, "alcohol-free" was defined as ≤ 0.50 % ABV. For each prepared ABV, the addition of the corresponding amount to base beer was replicated four times: this gave one control sample without any hop pellets but alcohol-adjusted ("N0", "L0", "M0" and "H0") and three samples including the Solero pellets at dry hopping ("N1-N3", "L1-L3", "M1-M3", "H1-H3"). In addition, one base beer without any adjustments at all was kept as a blank control ("base beer") for the calculation of transfer rates. The whole set-up resulted in a total of 17 individual trials, shown in table 2.

In order to avoid any microbial contamination (especially in the low ABV samples), the natural preservative Nagardo© was added to all of the 17 single trial beers [10].

The following observations and conclusions are made on the basis of the corresponding mean values. Single analytical results are not necessarily shown in this excerpt, but in the full study [6]. Transfer rates and variations of single components are demonstrated in relation to the increasing ABVs.

Non-volatile hop components and IAA

Fig. 1 gives an overview of the changes of non-volatile hop components if dry hopping was applied at varying ABVs.

Hardly any change was observed for the iso-alpha acids (IAA) although a certain decrease was expected after dry hopping [11]. Even at the highest ABV the drop is still within the analytical variation. In our study IAA can be assessed as unchanged after dry hopping and as being unaffected by alcohol concentration. In contrast, all other hop bitter components increased after dry hopping and, in some cases, also depending on the alcohol.

Alpha acids

The major increase was detected for the alpha acids (AA). For the N-beers, already 12.7 mg/l were introduced after dry hopping. They peaked at 61.5 mg/l in case of the H-beers, resulting in an increase of 370 % (fig. 1). Higher ABVs resulted in significantly more hydrophobic AA that were extracted from hop pellets and finally detected in the beer. The corresponding transfer rates were 6.4 % for the lowest and 32.3 % for the highest alcohol content (table 3).

Humulinones

After dry hopping, the humulinones (HUM) were detected in concentrations of 2.0 mg/l in the N-beers and 3.0 mg/l for the L-, M-, H-beers. These values resulted in unexpected low transfer rates of only 41.4 to 69.2 % (ta-

CHARACTERISATION OF HOP PELLETS USED

SOLERO aroma variety (crop 2020)	Method [7]	Type 90 pellets
LCV	EBC 7.5	10.1 %
Alpha acids	EBC 7.7*	8.8 %
Beta acids	EBC 7.7*	6.1 %
Humulinones	EBC 7.7*	0.2 %
Xanthohumol	EBC 7.15*	0.8 %
Polyphenols	EBC 7.14	5.7 %
Total oil content	EBC 7.10	1.1 ml / 100g
b-Myrcene	EBC 7.12*	56.0 % rel.
b-Caryophyllene	EBC 7.12*	4.8 % rel.
a-Humulene	EBC 7.12*	6.4 % rel.
Farnesene	EBC 7.12*	< 1.0 % rel.
Linalool	EBC 7.12**	0.7 % rel.
Geraniol	EBC 7.12**	0.4 % rel.

** the most recent international standards or pure substances were used for the calibration*
*** also based on EBC 7.12*
Table 1

TRIAL SET-UP SHOWING DRY HOPPING AND ETHANOL DOSAGE (IF ANY)

Samples	ABV (%) [8]	ABV adjustment ?	Dry hopping applied?
Base beer	0.4	No	No
N0	0.5	Yes	No
N1–N3	0.5	Yes	Yes
L0	3.5	Yes	No
L1–L3	3.5	Yes	Yes
M0	7.0	Yes	No
M1–M3	7.0	Yes	Yes
H0	10.5	Yes	No
H1–H3	10.5	Yes	Yes

Table 2

TRANSFER RATE (%) OF NON-VOLATILE HOP COMPONENTS

	Alpha acids	Beta acids	Humulinones	Xanthohumol
Samples	% transfer rate			
N1–N3	6.4	0	41.4	7.5
L1–L3	17.5	2.2	61.2	19.5
M1–M3	23.2	3.4	67.3	20.8
H1–H3	32.3	6.4	69.2	24.7

Table 3

ble 3) although higher transfer rates were reported in recent studies [12]. The higher contents of alcohol in the L-, M- and H-samples did not change the concentration of HUM significantly. It can be concluded that HUM are not affected by the alcohol content of the dry hopped beer.

Beta acids

Hydrophobic beta acids (BA) were also investigated. Even at an ABV of 3.5 % there was a clear improvement in the solubility, which resulted in a concentration of 3.1 mg/l. At higher ABV, this value was further increased by up to 8.4 mg/l for the H-samples. Concentrations at this level are very rarely found in regular beers because nonpolar BA are generally regarded as insoluble in beer [13]. In any case, transfer rates remained at a low level below 6.4 % (table 3).

Xanthohumol

Xanthohumol (XN) was hardly detectable in the base beer and any increase observed is exclusively attributed to substance transfer from pellet to beer after dry hopping. It is well known that XN is almost insoluble in water and ethanol is an ideal solvent [14]. Already an ABV of 3.5 % of the L-beers clearly improved the solubility of XN, demonstrated in fig. 1. The highest concentration of 4.3 mg/l was detected in the H-samples, which is about one quarter (24.7 %) of the XN introduced by dry hopping (table 3).

Bitter units

As a consequence of dry hopping, the bitter units (BU) increased and peaked at the highest ABV. The BU method primarily covers the determination of IAA at the used wavelength, but the hop components mentioned above also have a certain adsorption at 275 nm [7]. Since the IAA are practically constant in this trial, any increase above the originally measured BU of 9.4 of the base beer can be attributed to the additional concentrations of hop acids after dry hopping, primarily the AA but also dissolved HUM and BA. Indirectly the BU are therefore “ABV-dependent”, as introduced poorly soluble bitter substances show better solubilities with more ethanol added.

Hop aroma components

Hop aroma substances were measured according to Schmidt et al. [7, 15]. Table 4 shows the averaged values of each ABV-group. In most cases, the individual results varied within or close to the analytical tolerance (± 10 %) with a few exceptions [6].

Ketones

The absolute level of investigated single ketones remained below 50 µg/l, with the two ketones 2-undecanone and 2-dodecanone were found to have clearly reached their highest values in the H-samples (table 4). In contrast to these two ketones, 2-decanone seems to be extracted more evenly and within a smaller range. In general, the concentration of ketones increased to a certain plateau at 3.5 % ABV already. There is a clear dependence between better solubility at higher ABVs.

Esters

Four hop-derived esters were examined. Comparing the base beer with the N-samples, each component was clearly transferred to beer after dry hopping. 46 to 70 % of the highest amount detected within any ABV group were already found in the corresponding N-samples. The best extraction at only 0.5 % ABV was found for isobutyl isobutyrate (70 %), followed by 3- and 2-methylbutyl isobutyrate (58 %) and 46 %

MEAN VALUES OF HOP-DERIVED AROMA COMPOUNDS IN µG/

		Base beer (no dry hopping)	N1–N3	L1–L3	M1–M3	H1–H3
	ABV (%)	0.4	0.5	3.5	7.0	10.5
Ketones	2-Undecanone	n.d.	14.7	30.0	28.3	44.2
	2-Dodecanone	n.d.	n.d.	19.6	18.9	33.6
	2-Decanone	n.d.	11.0	14.6	13.8	17.8
Esteres	Isobutyl isobutyrate	n.d.	166.3	238.5	238.3	237.5
	3-Methylbutyl isobutyrate	n.d.	16.1	26.4	27.3	28.0
	2-Methylbutyl isobutyrate	n.d.	160.1	261.2	266.0	277.0
	Geranyl acetate	n.d.	60.4	115.9	122.2	130.9
Terpene alcohols	Geraniol	n.d.	193.4	246.8	250.0	198.4
	Linalool	n.d.	195.3	213.0	204.0	214.5
	α-Terpineol	n.d.	19.7	30.1	22.9	22.7
Mono- and sesqui-terpenes	β-Myrcene	n.d.	708	13718	13974	13502
	β-Caryophyllene	n.d.	5.6	51.3	60.7	86.8
	α-Humulene	n.d.	7.6	55.9	77.2	102.8
	β-Limonene	n.d.	8.8	85.4	95.4	103.1

Color code
Lowest value after dry hopping (N-samples)
Increase compared to N-samples
Significant increase compared to N-samples
+ 100 % and more based on lowest values detected in corresponding N-samples

Table 3

in the case of geranyl acetate. This first initial leap after dry hopping demonstrates the excellent solubility of hop-derived esters, which can be beneficial for the aroma in dry-hopped NABs. At 3.5 % ABV, all components reached a certain plateau with values that already corresponds to the maximum concentration, or concentrations very close to this value. Above 3.5 % ABV, the hop esters are hardly dependent on alcohol.

Terpene alcohols

The terpene alcohols, geraniol and linalool, are known to have good solubility in beer even at low alcohol concentrations and this can be clearly demonstrated when comparing the N-samples with the base beer. After dry hopping, concentrations of almost 200 µg/l were already reached in the N-samples. In all other ABV-adjusted samples, concentrations above 200 µg/l were detected and at more or less constant plateaus with the exception of the H-samples of geraniol. The latter might be caused by a sampling error, as all other values indicate the maximum concentration was reached at 3.5% ABV and above. As there is only a small difference between N- and all other grouped samples, it can be concluded that ethanol additionally improves the solubility of most important terpene alcohols, but only to a certain extent.

Mono- and sesquiterpenes

Alcohol-dependent behaviour can be observed for all examined mono- and sesquiterpenes and results in higher concentrations the more ethanol added. Myrcene was clearly solved at an ABV of just 0.5%, but exceptionally high concentrations have been detected in all other samples with an ABV of 3.5 % and above. This high level of almost 14 000 µg/l can be explained by dosing hop pellets into a closed system and the use of a finished beer with very few yeast cells. There were no losses due to adsorption on yeast cells [16], which is usually the case when removing yeast and/or cold trub under regular production conditions. Both issues resulted in virtually no losses and explain the exceptional high levels, in particular for β-myrcene which is the major aroma substance in the hop's essential oils (table 1). Compared to the other shown mono- and sesquiterpenes, the level of β-myrcene is too high to still find a significant upwards trend in correlation with ABV. At concentrations below 10 µg/l, β-caryophyllene, α-humulene and α-limonene were barely soluble at an ABV of 0.5 % but concentrations clearly increased at 3.5 % (in two cases by approx. a factor of 10) and continued upwards with increasing ABVs. Hence, their peaks were observed in all corresponding H-samples and it clearly demonstrates that ethanol is beneficial for the solubility of mono- and sesquiterpenes.

Conclusions

This study demonstrated the analytical impact of ABV on dry-hopped beers. A variation in the alcohol content (0.5 to 10.5 % ABV) resulted in different solubilities of hop-derived volatile and non-volatile substances. This information is crucial to understand substance transfer and to achieve consistent beer quality, also with regard to sensory aspects.

The main bittering compounds in dry-hopped beer (iso-alpha acids and humulinones) remained unchanged, whereas concentrations of the hydrophobic bitter substances (alpha, beta acids and xanthohumol) were significantly higher the more ethanol was added.

The ABV-dependent behaviour of the analysed groups of hop-derived aroma substances has been characterized. Significantly higher concentrations have been observed for mono- and sesquiterpenes as well as for ketones if the beers contained increasing alcohol contents. The terpene alcohols displayed hardly any ABV dependency and also the highly soluble esters could not be further increased by adding (more) ethanol. For the production of hop-forwarded NABs, the highly soluble terpene alcohols and esters can be particularly advantageous, as they behave hardly ABV-dependent. ■

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